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THE DEVELOPMENT OF PHOSPHATE-FREE HEAVY DUTY DETERGENTS

Anthony M. Schwartz, et al

Gillette Research Institute, Incorporated

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March 1974

THE DEVELOPMENT OF PHOSPHATE-FREE HEAVY DUTY DETERGENTS

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Program Element 1BB045

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ABSTRACT

The purpose of this project was to demonstrate state-of-the-art possibilities for producing phosphate-free household laundry detergents of satisfactory environmental and performance characteristics. The work involved formulation of several hundred experimental detergent compositions using different surfactant-builder combinations. These were tested for laundering performance, acceptability of physical form, biodegradability, aquatic toxicity, potential hazard in use, and growth stimulation of algae. Feasibility of economical production on an industrial scale was also considered. Some partially satisfactory formulations were arrived at, their shortcomings being with regard to performance and/or economic feasibility, the two factors that must in the immediate state-of-the-art be traded off. These formulations coincide remarkably with the formulations developed independently by the industry and offered in jurisdictions where phosphate-containing detergents are banned. Some new builders and surfactant-builder combinations showed considerable promise, but could not be completely checked out with regard to all stipulated characteristics. Further work with these novel materials is recommended, but only along environmental and health-hazard lines.

This report was submitted in fulfillment of Project Number 16080 FWE and Contract Number 14-12-875 by Gillette Research Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of November 30, 1973.

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CONCLUSIONS

1. The problem was to provide a phosphate-free heavy duty household laundering detergent having the stipulated environmental properties and consumer-acceptable laundering performance. The most immediately applicable technical solutions worked out in the course of this project are as follows:

   a. A detergent consisting essentially of a mixture of conventional surfactants substantially unbuilt, the surfactant content being in the range of 40% or higher, i.e., two or more times the surfactant content of current conventional phosphate-built detergents. This detergent would be liquid in form.

   b. A detergent consisting of about 25% conventional surfactant and 20-40% of silicate or mixed silicate-carbonate as a builder. The carbonate content of this mixture should not be higher than about 25%. This detergent would be solid.

   c. A detergent consisting of a mixture of conventional surfactants or special surfactants of high washing power together with sodium citrate or citrate and silicate as the builder. These detergents can be liquid or solid depending on the surfactant.

It is of interest that detergents in all three of these classes have been developed by the industry and offered in the marketplace in jurisdictions where phosphate-built detergents are banned.

2. Soap and soap-lime soap disperser combinations are not considered to offer performance of the type to which detergent users are accustomed. Even in moderately hard water a high concentration is needed to provide good soil removal, and the build-up of residues in the fabric can become objectionably high.

3. From the performance point of view NTA is a satisfactory substitute for phosphate. Its adoption in commercial product would appear to hinge on questions of possible hazard, outside the scope of this project.

4. The product beta hydroxyethyl iminodiacetic acid (abbreviated SHIM or HEIDA) appears to be a very promising potential substitute for phosphate. It has high building power and passes the stipulated tests for environmental acceptability. It appears close to the FDA and CPSC borderlines with regard to toxicity, and requires further testing on this point. It appears more suited to liquid than to solid formulations.

5. The product carboxymethyloxysuccinic acid (abbreviated CMOS) is a potential substitute for phosphate. In building power it is somewhat stronger than citrate, particularly with the most widely used surfactants, but not as strong as phosphate. Environmentally it appears acceptable.

6. The polymeric product POCNa, produced and offered in Germany as a substitute for phosphate builder, appears to have some potential as a phosphate substitute. It is relatively weak in building power, however, and possibly too slow in biodegradation.

7. Several other polymeric products appear to provide satisfactory building action and be at least partially biodegradable. Whether or not they are satisfactorily biodegradable has not yet been settled.

8. A large number of patents have recently issued and continue to issue on phosphate-free detergents that purport to be environmentally acceptable. Several of the patent examples have been partly investigated, and some show promise.

9. The concept of laundering with low concentrations of unbuilt, environmentally acceptable, non-hazardous surfactants, in water softened by in-situ ion exchange resins, has been cursorily explored. It is proposed as a concept worthy of further investigation.

10. The satisfactory replacement of current phosphate-built detergents by environmentally acceptable non-hazardous phosphate-free detergents of substantially equal performance is a very difficult economic problem as well as a technical problem. Technical answers appear to be near realization, although the complete establishment of environmental acceptability and lack of hazard is a long and difficult task (cf. NTA). The necessity for a trade-off between cost and performance must be realized, since phosphate is a relatively inexpensive commodity. Furthermore, the economic dislocations and the time involved in effecting such a replacement would under the best of circumstances be formidable.

RECOMMENDATIONS

In view of the findings of this project, summarized in the DISCUSSION and CONCLUSIONS sections of this report, it is recommended that:

1. Performance and/or sponsorship of experimental work directed explicitly toward the formulation of phosphate-free detergents be discontinued. This relates especially to the measurement and improvement of laundering performance.

2. The detergent industry and its suppliers be encouraged to develop complete data on the environmental and hazard characteristics of new non-phosphate detergent formulations and their essential ingredients.

3. Full cooperation in this endeavor be offered with regard to stipulating the various characteristics and establishing test protocols and standards of acceptability for them.

INTRODUCTION

When this project was started in the summer of 1970 essentially all of the heavy duty household laundering detergents marketed in the U.S.A. contained as a necessary ingredient a substantial proportion of sodium tripolyphosphate. The potential ecological hazards of this material and other phosphorus compounds had been recognized, but no generally acceptable phosphate-free laundering compositions had been developed to the stage of commercial feasibility. The objective of the project accordingly was to formulate a phosphate-free heavy duty household laundering detergent which would be:

a. satisfactorily biodegradable.
b. non-stimulating to undesirable algae.
c. non-toxic to fish and representative lower organisms in fish food chains.
d. safe to use and to have in the household.
e. satisfactory to the consumer in its performance.
f. economically feasible to produce and market on a scale comparable with that of currently used phosphate-containing detergents; i.e. industrially and commercially feasible.

This was intended essentially as a demonstration program. The aim was to find out if such a product could be made using known materials and existing technology. It was understood that there could be no compromise with either the environment or product safety requirements (items a-e). These could be clearly defined in terms of test protocols, and no inordinate difficulty was anticipated in reaching agreement on such protocols. Industrial feasibility and satisfactory performance, however, are not so easily defined and agreed upon. With regard to these items the following stand was adopted.

Industrial feasibility implies that raw materials are adequate and production processes sufficiently developed to allow reasonably early production in the million-ton per year range. Judgment of industrial feasibility is based partly on our knowledge of the chemical industry and partly on assurances of those offering the candidate materials. Commercial feasibility is based on two factors, cost and performance. Performance is in turn made up of a large number of sub-factors which the household consumer considers in making her final judgment of acceptability. These include not only soil removing power (the factor usually weighted most heavily) but also convenience of physical form, rapid solubility at laundering temperatures, no adverse effects on fabrics or washing machine, etc. It is in the cost and performance factors where some flexibility is allowable (in fact, inevitable) and where trade-offs can be made. Just as there are several different types of commercially successful phosphate detergent, we visualized more than one type of phosphate-free detergent as being able to make a commercial success in the forced absence of phosphate.

It was realized that practically all the important units of the industry, producers, and suppliers, were working intensely toward the same goal as we, and that during the course of the project many phosphate-free formulations were likely to appear in the market. It was planned to monitor such products and to examine them carefully. Any product that met the above requirements would be considered an answer to the objective of the program even though it did not stem from our own organization. In accordance with this approach it was also planned that we keep fully abreast of announced developments and follow up on any that appeared meritorious. We could thus be regarded not only as researchers seeking to develop a new product but in a limited sense as surrogate consumers assaying the suitability of products that might appear from other sources.

PROGRAM DESIGN

A. LIMITATIONS ON MATERIALS SELECTED

To be considered as candidate detergent ingredients (surfactant, builder or auxiliary) the materials used in this program had to meet certain economic and commercial requirements relating to cost and availability. Furthermore, certain types of auxiliary ingredients have been excluded from the study entirely. Among the more important items in this latter category are enzymes, bleaches (both peroxygen and chlorine types), brighteners, fabric softeners, emollients, anti-tarnish, anti-caking and anti-dusting agents. The mission was to find a non-phosphate formulation that performed like the phosphate-containing ones. Phosphate contributes, along with the surfactant, to true physical removal of soil; and therefore this was the key performance effect we studied. Enzymes and bleaches remove soil by chemical rather than physical action. Brighteners contribute only the appearance of soil removal. The other ingredients are not only unrelated to soil removal but are unaffected by the presence or absence of phosphate. Thus the ingredients of interest in this study were surfactants, builders, anti-redeposition agents, and any other materials (solvents, inorganic detergents, etc.) that might contribute to physical soil removal.

The economic requirements were somewhat more difficult to pinpoint. As mentioned above, it was not considered likely that a replacement formulation could be found equal in cost efficiency to the phosphate detergents. The objective was to minimize the sacrifice that would have to be made in cost efficiency, and to satisfactorily balance the cost factor against the performance factor. The performance can be, and was, measured in the laboratory with some precision. Costs are more difficult to estimate unless one is actually in commerce, ready to negotiate firm purchase and sales contracts. They can be estimated with reasonable closeness, however, if the process of manufacture is known, by extrapolation from raw material costs, or from present prices if the material is now being made on a limited scale. Almost as important as the cost is the potential availability of the candidate material on a large scale. Detergent phosphate is used at a rate of well over one million tons per year, and detergent compositions at a rate of over three million tons per year. The only materials considered seriously were those that seemed potentially available in the million ton per year range at a cost not too far removed from present detergent component costs.

Cost is of special importance when considering the builder alone rather than the whole detergent formulation. Many surfactants (soap is possibly the best known example) can deliver good laundering performance if used at sufficiently high concentration. In such cases, the builder must be less costly than the surfactant for a builder-surfactant combination to make economic sense.

No formal limitation was placed on the source of the experimental materials. Most of the surfactants were available as items of commerce, although a few were submitted as development samples by established surfactant manufacturers. Most of the builders were in the category of development samples from established chemical manufacturers. A very small proportion of the builders were synthesized in our laboratories, in most instances to establish guidelines on the relationship between chemical structure and detergent building effect. It was an explicit policy to avoid or at least minimize the use of newly synthesized compounds, because the complete proving of safety, performance and feasibility would take too long a time. Primary attention was given to materials about which such information was available.

B. LIMITATIONS ON CONSUMER ACCEPTABILITY

To gain customer acceptance a detergent product must meet certain requirements with regard to physical form. Suspensions or emulsions that tend to settle or break in the package are not considered acceptable. Powdered or beaded products that sinter to a solid cake or deliquesce are similarly unacceptable. The paste form, although acceptable for industrial detergents, is not favored for household use. Acceptable forms include the spray dried bead, dry blend coarse powder, tablet, and liquid. We did not undertake to produce the formulations in their final ready-to-package physical form. We did determine, by drum drying, whether stable solid non-hygroscopic, non-caking forms could be produced. We also determined whether our formulations could be made into stable liquids of adequately high concentrations. No attempts were made to produce any of the formulations in tablet form.

An experimental liquid formulation was not considered satisfactory unless it contained only one liquid phase and was sufficiently concentrated to match currently successful commercial liquids. Solid formulations were considered satisfactory only if they were non-caking, non-hygroscopic and free-flowing. Aside from these requirements relatively little emphasis was placed on the physical form of our formulations. Preferences in physical form, appearance, fragrance, etc. vary widely from one detergent manufacturer to another. They are greatly influenced by considerations of large scale production and marketing, and therefore we regarded the perfecting of physical form as a secondary rather than a primary requirement of the project.

C. SCOPE OF THE TESTING PROGRAM

To be considered satisfactory the final formulations had to pass tests in five different categories: 1) Algal stimulation; 2) Aquatic toxicity; 3) Biodegradability; 4) Hazard in use (human toxicity) and 5) Laundering performance. It is evident that such tests might be extended ad infinitum, and that the set of test protocols must be adopted on a more or less arbitrary basis. The tests specified in the contract were judged at the time of their adoption to be optimum selection within the budgetary and time limits of the project. During the course of the project they have changed relatively little, although some new tests have been added.

Basic protocols for the tests in all five categories are given in Appendix I. The algal stimulation test procedures were adopted from the provisional algal assay procedures ("PAAP") of the Pacific Northwest Water Laboratory, EPA, and were periodically revised to keep in conformity with PAAP revisions. The aquatic toxicity tests have remained unchanged throughout the course of the program and require little comment. It should be noted that although the results of the snail and fish tests are reported to two or three significant figures their reproducibility is sometimes no better than two or three fold. This is not uncommon in bioassays where the number of specimens is limited. The reproducibility of the diatom growth inhibition test is considerably better, but it merits no more than a second significant figure.

In a program of this character the testing of biodegradability presents a difficult problem. Even under the most favorable circumstances it is difficult to determine the ease with which an organic compound will be oxidatively consumed by microorganisms in a natural (stream) or artificial (sewage plant) environment. The usual procedure is to follow the disappearance of the test material by direct chemical analysis. This requires an analytical method that is reliable in the parts per million range. Such analytical methods were not available for the great majority of surfactants and organic builders of interest in this program nor was it feasible to develop them. Another difficulty in testing for biodegradability is that the distribution of microorganism species in the inoculum or "seed" that is used differs greatly from source to source. A third major difficulty is that almost all seeds must undergo a period of acclimation before they can attack an organic material that is new to them, even if that material proves ultimately to be biodegradable. Contrariwise, by careful acclimation microbes can be nurtured and developed to oxidatively consume almost any organic material, even some that are considered germicides. There is accordingly much arbitrariness in specifying an acclimation procedure and a source of microbes.

Except in those few cases where analytical methods were available we used the biochemical oxygen demand (BOD) to indicate aerobic biodegradability, comparing it with the chemical oxygen demand (COD) and with the BOD of standard compounds known to be readily biodegradable. A variety of acclimation conditions and procedures were used when necessary. Similarly, a variety of different sludge sources were tried in cases where the first one tried (EPA experimental sewage disposal unit in the District of Columbia) failed to initiate biodegradation.

The estimation of hazard in use is another area in which compromises and arbitrary decisions must be made in setting the procedure. At the start of the program five tests were specified and written into the contract: acute oral toxicity on rats, acute dermal toxicity on rabbits, opthalmic irritation on rabbits, primary skin irritation on rabbits, and primary skin irritation and sensitization on humans.

Food and Drug Administration protocols were used. Relatively early in the course of the project controversy over the possible teratogenic and carcinogenic effects of NTA received much public attention. At a somewhat later date similar concern was expressed over possible esophageal damage by excessively alkaline detergents. It was decided not to perform any tests of carcinogenesis or teratogenesis on candidate formulations, but to include a test for esophageal damage. The test adopted was a provisional test, utilizing rabbits as the test animal, provided by the Bureau of Product Safety, FDA. Obviously, materials such as NTA, that have been objected to for properties we do not assess, were excluded from the program.

Tests with regard to laundering performance can be extended almost indefinitely and can be the subject of much argument. The test with which we started and the rationale for adopting them were set forth in the original proposal and incorporated into the contract. They are outlined in Section I of Appendix B. The major points guiding their adoption were: 1) that true soil removal and soil redeposition should be the parameters of interest rather than optical effects due to brighteners; 2) that foaming was of minor importance, except insofar as a too persistent foam might indicate poor rinsability; 3) that effects on the fabric, including ash build-up and the build-up of organic residues, were important parameters of performance. During the course of the project a low level but continuing effort was devoted to checking, extending and modifying the test methods with a view toward greater accuracy (accuracy here means the extent to which the tests correspond with results obtained in actual practice) and more general acceptability. It should be pointed out that there are at present no standard laboratory tests for rating on an absolute basis the soil removing power of laundry detergents. Each manufacturer of these products has his own set of protocols, and the accuracy of any single simple test procedure is not easy to defend. Our methods development work and its adoption in the overall program is presented in Appendix B.

D. PLANNED TECHNICAL APPROACHES

Keeping in mind the scope and the limitations outlined above it was planned to divide the experimental work into three main areas. The first and most important area would be the actual preparation and testing of new detergent formulations. From the formulations would ultimately come the new formulation we were seeking. The second area of investigation would involve the chemical analysis and performance evaluation of existing commercial detergents that appeared to be of interest. A large number of new detergents appeared in the market during the course of the project. A knowledge of their composition and their laundering performance was obviously of utmost importance to the project. The third area of experimental work was to be concerned with methods development. As mentioned above there was perforce a considerable degree of arbitrariness in the initial selection of test methods. We realized from the beginning that the methods would probably require modification as the experimental work proceeded and that the methods most likely to require modification would be those relating to laundering performance.

The examination of existing products and the development of more effective and realistic test methods required little advance planning. The formulating and testing program however had to be carefully planned even though, as in all R and D work, these plans would have to be continuously modified and reoriented on the basis of incoming results. We can consider the plan in two separate parts, a formulations part and a testing part.

Detergent formulations can be grouped into three large classes. First, those that are based on straight surfactant; second, those that are based on surfactant plus a precipitating builder; and third, those based on a surfactant plus a non-precipitating or chelating builder. This third class is represented by the conventional tripolyphosphate built detergent. In all three of these classes, it is understood that the formulation can and usually does contain a certain amount of silicate as an anti-corrosive agent. This usually constitutes 5 to 10% of the total mixture. It also contains in the range of .5 to 1.5% sodium carboxymethyl cellulose as an anti-redeposition agent and may contain similarly small amounts of other anti-redeposition agents that are supposedly more effective on the non-cellulosic man-made fibers. The formulation may also contain fillers and standardizing materials, usually sodium sulfate, as well as minor amounts of brightener, perfume, color and other adjuvants. We shall consider in this discussion only the surfactant and the builder, assuming that the other ingredients will be present as required in the final formulation.

It is generally recognized that straight synthetic surfactants, unlike soap, are poor in cotton washing. Historically this is the reason that the market for synthetic surfactants remained quite limited until the discovery of the specific building effect of the condensed phosphates. It is also known, however, that this inferior cotton washing property varies considerably from surfactant to surfactant. LAS, the most commonly used surfactant, is a mediocre cotton washer. Soap is notably good. We planned to explore systematically the cotton washing powers of a range of surfactants, paying special attention to those claimed to wash well in the absence of builders. We refer to these for brevity as "supersurfactants." Testing would be limited of course to supersurfactants that appeared economically feasible. It was also planned to test mixtures of soap with various lime soap dispersing surfactants.

Such compositions have been widely mentioned from time to time as possible substitutes for phosphate formulations in heavy duty laundering, and they have been used in bar toilet soaps for personal use.

The theory of detergent action teaches broadly that the cleaning or deflocculating effect of the surfactant is opposed by the presence of polyvalent metallic cations in the solution, calcium ion being the commonest and most important offender. Possibly the most important action of a builder (although by no means its only action) is to remove calcium ions from solution. One of the ways in which the builder may do this is by precipitating the calcium as an insoluble compound. The best known example of such an effect is the use of sodium carbonate as a builder, the sodium carbonate precipitating out calcium ion and thereby allowing the surfactant to do its work. Despite the first order simplicity of this theory it is known that the building effect of sodium carbonate varies greatly from one surfactant to another. Formulations based essentially on a non-ionic surfactant plus a very high proportion of sodium carbonate were introduced on a large scale not too long after experimental work on the project started. Due to their high alkalinity these materials appeared to have certain drawbacks with regard to safety in use, and were therefore not considered ideal answers to the problem of developing a phosphate free detergent. At a later date household detergents containing a lower proportion of carbonate, usually with an equivalent amount of silicate, were introduced in the market. At about the same time there appeared detergents containing little or no carbonate, but a high proportion of silicate, in the range of 20-25% of a high silica-to-soda ratio material. This material has building properties although it is neither strictly precipitating or sequestering. The carbonate and silicate built materials will, however, be grouped together for purposes of discussion.

The non-precipitating or sequestering builders remove calcium ion by chemical reaction without forming a precipitate. The prototype of such builders is of course sodium tripolyphosphate. The main thrust of the program involved finding and formulating new builders of this type.

Relatively few non-precipitating builders had been extensively explored, or if they had been the information was not publicly available. The big exception was NTA which had not only been quite thoroughly explored, but had been used on a limited commercial basis and was generally considered to be the logical successor to the condensed phosphates. Because of certain limitations with regard to physical form and large scale manufacture, however, it was stated at that time that NTA could be used only as a partial replacement for phosphate rather than a complete replacement. A considerable number of other possible candidates were known but virtually nothing was known of their actual effect in practical formulations. It was strongly suspected that the building effect of these materials would vary depending upon the surfactant with which they were combined, i.e., certain of these builders might be very effective with some surfactants but ineffective with LAS (the commonest and least expensive synthetic surfactant but one of the more difficult to build). It was planned to solicit such materials from chemical companies that were willing to supply them and to test them with a variety of surfactants. It was also planned to synthesize builders of this type which might appear to be particularly promising, provided they could not be obtained from primary chemical manufacturers. It was not envisioned, however, that such synthesis would constitute a major proportion of the program. We did not consider that the invention of new builders was our primary mission, and intended to resort to it only when necessary.

It was planned to make up the formulations for launderability testing without actually putting them together, i.e., the ingredients in proper proportions would be put into the wash liquor without pre-mixing. A separate aspect of the program would be undertaken for those combinations of ingredients that performed well. This would involve putting together the ingredients into a final formulation which would have to have the acceptable physical characteristics mentioned above.

It was realized that the testing program, involving five different types of tests, could not be well planned in advance but would have to be organized on an ad hoc basis. The reason for this was the discrepancy in the times required to carry out each test. A chronic aquatic toxicity test, for example, may take as much as a year to complete whereas a soil accumulation test takes only about three days. In general, the laundering evaluations were conducted first. Biodegradation and algal stimulation tests followed in that order. Materials that looked promising in these tests were then submitted for acute aquatic toxicity tests. Product safety tests and chronic aquatic toxicity tests, as well as bundle tests for laundering effectiveness were only conducted on formulations which were entirely satisfactory from all other points of view. These tests are by far the most time consuming and expensive.

It was planned in the testing program to make full use of all the information that could be obtained either in the open literature or from the suppliers of the candidate materials. Checking the validity of such previously available information is considerably less time consuming than developing it from scratch.

EXPERIMENTAL

The basic soil removing formulations being sought were visualized as consisting either of surfactant alone or of surfactant plus a non-phosphate builder. The candidate materials entering the program were accordingly either surfactants or builders. Depending on the information available, these materials might be tested first for biodegradability or aquatic toxicity or they might be made up into a formulation and given the preliminary tests for laundering effectiveness. Throughout the program most of the major areas of investigation were being worked on simultaneously. Whenever a material or a formulation failed definitely to meet any of the important requirements it was dropped from further consideration. For efficiency in the program the simpler tests were usually conducted first, and the more time consuming tests later on the successful candidates.

A. FORMULATING AND WASH TESTING

A total of several hundred different formulations were made up and wash tested during the course of the program. For purposes of discussion they can be grouped into eight classes, based on the type of builder used, as follows:

1. Unbuilt surfactants. It is well known that surfactants differ from one another in their washing power. They also differ in their response to any given builder. Candidate surfactants were generally tested by themselves to see if they were unusually effective

and might be made the basis of a completely unbuilt formulation. Soap and mixtures of soap with lime soap dispersing agents (which are themselves surfactants) are included in the cateogry of unbuilt surfactant formulations.

2. Carbonate and/or silicate-built formulations. Carbonate was a standard builder for soaps and also for synthetic surfactants before the advent of condensed phosphates. It is a precipitant for calcium ion rather than a sequestrant. A relatively small proportion, usually 8%, of a high ratio silicate (2:1 to 3.22:1) was included in all our formulations to serve as a corrosion inhibitor. This is common practice in detergent formulation. Higher quantities (up to 40%) have been recommended as builders and as adjuncts in combination with other builders. We tried them in both ways. Silicates having an SiO_2 to Na_2O molar ratio less than 2:1 were not used because their high alkalinity was considered too great a hazard in use.

3. NTA. At the start of the project NTA was regarded as the candidate builder most likely to prove satisfactory and be adopted by the industry. Its properties were therefore checked. No work with NTA was done after the controversy developed over its possible hazards.

4. An analog of NTA was submitted as a candidate builder early in the program. This compound, code named SAND, contains an acid amido group ($-CONH_2$) in place of one of the carboxyl groups of NTA. This was tested to a limited extent, but later in the program was deemphasized in favor of another NTA analog described below.

5. The material code named SHIM or HEIDA is the di-sodium salt of βhydroxyethylimino-diacetic acid. This material was tested very extensively. SHIM is the earlier code name. HEIDA is the more recent name coined by the supplier. Both names are used in this discussion,

SHIM referring to earlier samples and HEIDA to more recent ones. There appears to be no significant differences between them.

6. Formulations based on organic polymeric builders. It was known at the start of the program that certain water-soluble polycarboxylated polymeric materials, of both natural and synthetic origin, were builders of the sequestering type. A considerable number of these were explored and several were later tested intensively. They included only compounds containing no elements other than C, H and O.

7. Formulations based on monomeric sequestering agents containing only C, H and O. Citric acid (as sodium salt) and carboxymethyl oxysuccinic acid (abbreviated CMOS) were the most extensively tested.

8. A system of washing with unbuilt surfactants including an ion exchange resin in the bath to sequester the hardness was explored in a preliminary manner.

The initial procedure for estimating the laundering potential of a new compound was as follows:

If the compound was a surfactant it was made up into a formulation containing 12 - 25% active surfactant, 8% sodium silicate, 1% sodium carboxymethylcellulose (NaCMC), 0 - 50% (sometimes more) builder, and enough sodium sulfate to bring the total to 100%. The exact percentage of surfactant used depended on its chemical composition and on the type of surfactant against which it was being compared. The magnitude of the cleaning effect without builder was often a useful index of the value of the surfactant in combinations. The selection of builder and the percentage used varied, depending on the surfactant and the information being sought. The two surfactants used most often as standards of comparison were our standard LAS sample and a widely used fatty alcohol ethoxylate coded 68-127.* The LAS was usually used at the 20 to 25% level in its formulations and the 68-127 at 12%. New surfactants being compared against them were used at corresponding levels.

If the compound of interest was a builder it was in most instances tested with at least three surfactants, two of them being LAS and 68-127. The third and other surfactants would be those of specific interest in connection with the builder being tested. The formulations generally contained 12% of 68-127 or 25% LAS or an appropriate percentage of whatever other surfactant was being used. In practically all instances the formulations contained 8% silicate and 1% NaCMC. The percentage of builder was most often 30%, but 20% or 50% was sometimes used. In the primary launderability tests 0.3% total formulation was used in 200 ppm hard water. If the calcium sequestering power of the builder was known a high enough percentage (20% or 30%) was used to take care of the hardness. If the calcium sequestering power was unknown, and/or was suspected of being low, 50% was used. In the later stages of the program experimental builders were routinely tested for calcium sequestering power. This was done by titrating with a standard solution of calcium chloride, using an Orion Research, Inc., Divalent Cation Electrode model 92-32 to monitor the calcium ion concentration. The general procedure was to start with 100 ml of 2×10^{-3} molar calcium chloride solution (equivalent to 200 ppm hardness as $CaCO_3$) and titrate into a 2% solution of the sequestrant. Typical titration curves for strong v. weak and high efficiency v. low efficiency sequestrants of interest are shown in Figures 46-49.

(*See Appendix C for description of coded materials.)

The primary launderability test used throughout most of the program is described in Appendix B. Four cycles of soiling and washing were used; and four soil-fabric combinations: dry vacuum cleaner soil and sebum soil on cotton and a 50:50 cotton polyester blend finished for durapress (permanent press). Earlier straight polyester (unfinished) was also used as a test fabric, and some 65 polyester: 35 cotton durapress finished fabric was also used. The launderability behavior of these fabrics was sufficiently close to that of the 50:50 blend to justify dropping them, and devoting the time saved to examining more detergents. The AATCC #124 and AHAM detergents were used as standards, together with any other comparison detergents that were considered appropriate to the specific test. The reflectance readings were automatically transferred to punched tape which was fed to a computer. The computer was programmed to print out not only absolute reflectance readings but also the differences in reflectance between the test detergent washed swatches and the standard detergent washed swatches. These differences, or "delta values", greatly facilitate comparison. Their significance can be judged on the basis of their statistical confidence limits, also printed out by the computer but not included in the tables of this report. In most of the runs shown in the tables delta values less than one unit do not indicate a difference that would be significant in practice. Modifications of this primary multicycle test are detailed in Appendix B. Table headings indicate which of the tests was used to obtain the data in the tables.

Aside from the primary multicycle tests three other tests for launderability were used. These tests were applied mainly to the more promising formulations. They were: single cycle detergency v. concentration tests using purchased cotton soil cloth (Empa); single cycle detergency v. concentration tests on cotton and blend soil cloths prepared in this laboratory ("Colgate" soil); and the bundle tes (ASTM D-2960-71T). These are described in Appendix B. Data from the single cycle tests are shown in the Figures as plots of soil removal v. detergent concentration. Some of the multicycle tests were extended to include a range of detergent concentrations less than the 0.3% used in screening. Data from these tests are also presented in graphic form. Data from the bundle tests are included in the text of the sections headed RESULTS and DISCUSSION respectively. In many instances launderability tests were performed at water hardnesses other than 200 ppm. This is indicated in table and graph headings and in the Text.

In all tests for launderability, including single cycle, multicycle, and bundle tests (except where specifically noted), redeposition swatches were included and measured. The data accumulated on redeposition is therefore fully as voluminous as the data on soil removal. It did not at any point, however, present any anomalies nor did it differ from what might have been expected on the basis of the soil removal results. It is therefore omitted from this report on the basis that any added significance it might contribute would not justify the excessive space required.

B. PHYSICAL FORM

Experimental work directed toward producing formulations of commercially acceptable physical form was necessarily limited. The ability to produce a beaded solid form of detergent on a large scale cannot be guaranteed by laboratory scale experimentation. We had available, however, a laboratory size drum drier (sometimes referred to as a roller drier), and the behavior of materials in this equipment can usually be extrapolated with confidence. In particular, drum drying on a laboratory scale can indicate very well whether the formulation will be hygroscopic, or have a tendency to sinter or become compacted, or have other unacceptable faults. Liquid formulations that are satisfactory when made on a laboratory scale usually present no difficulty in large scale operation.

The only formulations that we tried to put together in assembled form (solid if possible; liquid if a satisfactory solid form could not readily be made on the drum drier or by dry mixing) were those that appeared most promising in the primary launderability tests and had not been rejected in any of the other tests. These included SAND and SHIM formulations, silicate-citrate formulations and NTA formulations. The NTA formulations were developed during a period when eventual NTA acceptance (from the hazard-in-use point of view) was considered highly probable. In preparing the dry formulations the ingredients were dissolved or slurried in a sufficient amount of water to enable easy transfer to the hot drums, and were thoroughly mixed while transferring to assure homogeneity. No lengthy hot crutching, common in large scale spray drying operations, was used; and the possible effects of such treatment were not determined.

C. EFFECT ON FABRIC

Detergents that contained large proportions of soap and/or of carbonate, and that had proved promising in preliminary tests were tested for effect on fabric as follows: Swatches of the fabric were put through a series of 20 to 50 washing-drying cycles with no intermediate soiling. They were then analyzed for ash content and for alcohol extractable content in the usual manner.

D. AQUATIC TOXICITY

Two types of aquatic toxicity test were included in the program: an acute test and a chronic or long term test. Both are described in Appendix A. All aquatic toxicity testing was done by the Department of Limnology, Academy of Natural Sciences, Philadelphia. The acute test was applied only to compositions that showed promise of good performance. Together with biodegradability and algal stimulation the acute aquatic toxicity test constituted the second level of testing to which candidate compositions were submitted.

The chronic toxicity test consists of an extensive series performed over a protracted period on a relatively large number of species. Only two compositions over the whole duration of the program were put through the chronic test protocols. These were the citrate-silicate-ether carboxylate composition identified as 64-1, and the control detergent AATCCWOB. It was considered necessary to test the latter compound because no literature exists on the aquatic toxicity of well identified, typical, phosphate-containing, heavy duty household laundering detergents. The AATCCWOB detergent qualifies on all counts and can therefore provide a benchmark against which candidate formulations can reasonably be judged. Although the detergent with brightener would have been more realistic the brightener-free material was better suited as a standard of comparison for the brightener-free candidate experimental detergents.

E. BIODEGRADABILITY AND ALGAL STIMULATION

Tests for biodegradability and stimulation of algal growth, like the acute aquatic toxicity tests, were applied only to candidates that showed promise of good laundering performance. The protocols for these tests are described in Appendix A.

F. HAZARD IN USE

Testing for hazard in use, as outlined in Appendix A, is lengthy and extensive. Very few of the materials and compositions used in the program were submitted to these procedures. Materials known to be hazardous were excluded from the program. Suppliers were requested to submit all data on hazard which they had, and, in the case of materials which looked especially promising from other standpoints, to develop as much valid acceptable data on hazard as was possible.

G. WASHING WITH ION EXCHANGE RESINS

The concept of using a suitable packet of cation exchange resin in the washing machine, to serve as a substitute for the phosphate builder component of the detergent, was first considered by the group working on this project about April 1971. Experimental work to demonstrate its feasibility was performed during the following two months and was reported in Monthly Reports Nos. 12 and 13 of this series dated June 10, 1971 and July 10, 1971 respectively. This work was not mentioned in the Interim Report dated January 7, 1972. It is included herein for purposes of record, and to serve as a basis for future work that might be undertaken along these lines.

It is well known that many surfactants, including some of the inexpensive ones commonly used in detergent compositions, give good washing performance at low concentrations in the absence of builder provided the concentration of Ca^{++} or other polyvalent metallic cations in the system is very low. It would seem, on this basis, that an efficient convenient water softener system would enable the householder to do her laundry with surfactant alone. The catch in this proposition is that the concentration of Ca++ must be very low, preferably less than 10^{-6} molar (0.1 ppm as $CaCO_3$) for LAS, and not more than about 5 ppm for the more effective surfactants. The amount of Ca++ introduced by the soiled fabric is often sufficient to exceed this limit even after it has become completely diffused into and diluted by the wash water. Until such time as it has become diffused, the concentration at the fiber surface where detergent action is occurring far exceeds this limit. We therefore must soften the wash water in the machine as the washing is taking place. There are at least two ways to do this. One would be to have an ion exchange unit mounted on the washing machine together with a pump to circulate the wash liquor through the unit. A simpler way, and one which could be used with existing washing machines, would be to put a cloth bag (or other sturdy porous container) of ion exchange resin beads into the wash liquor with the laundry load. Calculations indicate that the amount of resin necessary to soften the incoming water and take care of calcium ion from the fabric load would not be excessive, and the cannister or bag of resin should remain effective through several launderings. When spent (or after a stipulated number of uses) it could be regenerated with brine by the householder or turned in for regeneration in exchange for a fresh bag. To explore the feasibility of this idea EMPA cotton soil cloth, which behaves qualitatively (although not quantitatively) like cotton in soil accumulation tests, was washed in 200 ppm hard water with an unbuilt LAS formulation, with and without ion exchange resin present in the wash bath. The resin beads were contained in a sturdy cotton bag, which was stirred around in the wash liquor as part of the fabric load. The load of resin in each bag was 5 grams, corresponding to about 11 oz. in an ordinary 17 gallon washing machine. This is theoretically adequate to soften several batches of 200 ppm wash liquor before requiring regeneration. For purposes of comparison similar washings were performed using the unbuilt formulations in distilled water and using phosphate-built formulations in hard water, both in the absence of resin. The unbuilt formulations were also used in hard water in the absence of resin, and gave the expected poor soil removal. Two cation exchange resins were used, both in the sodium form: Dowex 50 W-X8, a sulfonic acid type; and Amberlite IRC-50, a carboxylic type.

RESULTS

The experimental data involve seven categories of properties: launderability, physical form, effect on fabric, aquatic toxicity, biodegradability, algal stimulation and hazard in use. They also involve eight different categories of compositions: unbuilt surfactants, carbonate/silicate, NTA, SAND, SHIM-HEIDA, polymeric builders, monomeric builders and ion exchange resins. It is obvious that not all compositions, nor even a representative of every category of composition, were examined with regard to all property categories. Some compositions were studied much more extensively than others and, due to changing priorities during the course of the program, it was not always the most promising compositions that received most attention. Among the property categories launderability provided the most data. For purposes of presentation the processed data are therefore organized from two different standpoints. Data on all of the properties except launderability (also referred to as washing power or soil removing power) are presented in single tables which show the results for individual compositions of several different categories. In the launderability category the data are partly tabulated, partly graphed and partly (bundle test data) presented in the text. By no means all of the formulations that were examined are reported in the tables. Omitted are those which failed badly in one respect or another at an early stage. Also omitted are those poorly characterized or otherwise failing to meet the requirements discussed earlier in this report.

Results of the screening program on launderability are presented in Tables 1-7. These tables are the product of considerable processing, abridgement and condensation of raw data obtained over a period of three years. The changes in washing procedure details that occurred during this period are explained fully in Appendix B, and each procedure is described. For convenience in following the presentation, however, the following explicit notes on column headings in the tables are given. Tables 1, 2, 3, 3a, 4, 5, 6, and 7 refer to the multicycle or soil accumulation washing procedures outlined in Appendix B as "procedures 4 and 5" or as the "dry soil" and "oily soil" procedures. In the column headings of these tables "vacuum soil" is synonymous with "dry" or "procedure 4" soil. "Sebum soil" is synonymous with "oily" or "procedure 5" soil. The "blend fabric" referred to is a 50:50 cotton-polyester sheeting finished for permanent press. It is also referred to at places in this report as "durapress" fabric.

These tables show only the "delta G" values against the AATCC standard detergent after four cycles of soiling and washing. These values are the difference in reflectance between the fabrics washed in standard detergent and those washed in test detergent, as measured on the reflectometer with the green filter in place. As shown in Appendix B, measurements were also made with the yellow and blue Bx filters and confidence limits and whiteness values were computed. Redeposition swatches were also included in the wash load. Their reflectances were measured and the data processed in the same way. The redeposition results have been omitted for the sake of brevity. There is of course a much smaller range of reflectance and whiteness values among the redeposition swatches than among the soiled swatches, and in ranking the formulations for overall laundering performance soil removal performance greatly outweighs redeposition performance. In practically all instances the redeposition behavior paralleled the soil removal behavior closely enough to have negligible effect on the ranking. Also omitted are delta G (and "delta BX") values against the AHAM standard detergent which was used in almost all the important runs, and against various commercial detergents (notably Tide XK and Sears non-phosphate detergent) which were used in a considerable proportion of the runs. In a large number of the earlier runs 100% polyester swatches were included with cotton and/or blend fabric. These data have also been omitted.

The delta G values in the tables represent the number of reflectance units difference between the standard-washed swatches and the test-washed swatches. A positive value means the standard-washed swatches were brighter; a negative value means the test-washed swatches were brighter. Values in different series are not directly comparable, because the intensity of soiling necessarily varies from series to series, although with care it can be held reasonably constant. Strong soiling generally leads to larger delta G values whether positive or negative.

The "Proportions" column gives the percentage composition of the formulation. The first number in line represents percentage of surfactant; the second number percentage of silicate. When no letters follow the silicate number it means that silicate G (Philadelphia Quartz Co.) was used. Letters indicate other types of silicate (all in this report from this same supplier). The third number is NaCMC, in all but a very few instances used at the one percent level. The fourth number is percent builder; and the last number percent sodium sulfate unless otherwise designated. If the surfactant is a mixture (as in items 16 - 18 in Table 2) the first two numbers give the percentage of each surfactant.

Tables 1a, 6a and 7a relate to "Spangler soil" ("procedure 3") three cycle soil accumulation runs, and show the "delta W" (delta whiteness) values on blend and cotton fabrics. Tables 7b and 7c give whiteness values and show results for all five washing procedures described in Appendix B. The calculation of "whiteness" from the primary reflectance readings is also shown in Appendix B.

Studies of washing power (launderability or soil removal) of the various compositions tested as a function of detergent concentration are reported in graphic form in figures 1-36. Most of these studies were made with the Colgate soil, also referred to as "procedure 2" in Appendix B. Some were made with Empa cotton ("procedure 1") and some by the Spangler soil multicycle procedure ("procedure 3"). The procedure in each case is shown in the legend.

Data on physical form are shown in Tables 8 and 8a. All of these were developed during the first half of the program. As the program developed it was realized that commercially satisfactory forms might be capable of development in large scale equipment by experienced manufacturing organizations, even though they could not be made in our limited laboratory facilities. Emphasis was therefore placed on those other properties of the formulation that could be more realistically assessed.

Work performed with respect to effect of the formulations on the substrate fabric was also limited and is summarized in Table 13.

Acute aquatic toxicity data are summarized in Table 10. The complete reports on the two chronic aquatic toxicity tests that were performed, one on Formulation 64-1, the other on the control high-phosphate detergent AATCCWOB, are presented separately as Appendix E.

Estimates of biodegradability are presented in Table 11. As explained in Appendix A these estimates are based on BOD and COD tests and therefore relate only to aerobic biodegradation. A definitive study of the biodegradability of any single compound is in itself an extensive project, and even a complete study of BOD (varying temperatures, acclimation conditions, duration of test, etc.) is lengthy. The data obtained in this program, although quantitative and extensive, are considered too limited in scope to merit tabulation. The compounds and formulations are therefore grouped into three classes: those readily biodegraded in the test and therefore judged almost certain to biodegrade satisfactorily in natural waters and in secondary sewage treatment; those sufficiently resistant in the test to be judged unlikely to biodegrade in a reasonable time under the above conditions; those of intermediate resistance, on which extended studies should be made before judging their acceptability.

Data on algal stimulation are summarized in Table 9.

Data on hazard in use are summarized in Table 12.

All of the above tables and diagrams will be referred to in the presentation of results immediately following. The presentation is arranged according to composition categories.

A. UNBUILT SURFACTANTS

Referring to Table 1 it appears that relatively few straight surfactants, or surfactants built only with silicate, have a chance of washing satisfactorily at practical concentration levels.

The anionic sulfonates, particularly LAS, showed relatively little washing power in the unbuilt state (Items 60 through 66) even when used at the 25% level in the formulation. The same was true for the alpha olefin sulfonates (Items 31 through 35) and the ether sulfates (Items 36 through 42) although these were not tested at a level higher than 20%. The fatty alcohol ethoxylates, the most extensively tested surfactants (Items 19 through 21), showed increasing effectiveness on sebum soil with increasing concentration, but they still did not appear effective enough for practical consideration. One of the hydroxylated nonionics, Code 43-83, and the commercial detergent extract 32-237 did a creditable job at the 25% level particularly when built with excess silicate (Items 26 and 58). Possibly the most powerful non-soap surfactants in the unbuilt state were the sulfo zwitterionic materials (Items 52 and 55). Even these did not appear strong enough to be considered practical competitors for phosphate detergents.

The one material that appeared to wash as well as the reference phosphate-built detergent was soap. Item 69 indicates that a formulation consisting essentially of 85% low titer soap and 15% of a high ratio silicate washed about as well as the standard phosphate detergent. It must be borne in mind, of course, that both formulations are being tested at the same concentration, namely .3%, and that the standard phosphate detergent contains only about 20% active surfactant whereas this soap formulation contains 85% active surfactant. Item #70, which contains in addition to soap a substantial proportion of a lime-dispersing anionic surfactant, performed even better than the straight soap.

Continuing in Table 1a, LAS (items 81-84) and fatty alcohol ethoxylate (items 74-76) still appear significantly poorer than the control detergent even at the relatively high concentration of 27%. The mixture of fatty alcohol ethoxylate (FAEN) and fatty diethanolamide (items 79-80) appears better than the FAEN alone, giving another indication that mixtures of surfactants might be better than single species. The first such indication was the performance of the commercial detergent extract 32-237 (items 57-59 in Table 1). Surfactant 90-730 was stated by the supplier to be intended for use without phosphate, but in this test it proved distinctly inferior to the control detergent and about equal to unbuilt LAS. The soap-lime soap disperser (LSD)combinations (items 85-87) again showed superior launderability.

Detergency vs. concentration studies were performed on the more promising of these materials. Figures 1-4 show the results of tests on soap and soap-LSD combinations on Empa cotton soil cloth. In the 200 ppm water of this test all the soap-based compositions (at approximately 85% surfactant) were inferior to the control detergent (approximately 20% surfactant) up to .2% concentration. Above .2% the soap compositions performed better than the control detergent in this test.

The sulfonate zwitterionics' behavior on Colgate soil is shown in Figures 13-14. These materials performed remarkably well in a 30% ative composition, being especially effective in the concentration range under .15% and especially under .1%. These zwitterionics are not identical to those of Table 1, but they behave in a similar manner.

The behavior of two lime soap dispersing agents (used in the soap LSD compositions and purported to have good detersive properties when used alone) is shown in Figures 15-16. They did not fulfill expectations.

Surfactant 90-730 was tested extensively, not only against the control detergent AATCCWOB (Figures 5-6) but also against LAS in a comparable formulation (Figures 7-10) and against one of the more promising non-phosphate built compositions (Figures 11-12). On both Spangler and Colgate soils it exhibits the same behavior. It is superior to AATCCWOB at concentrations under .15% (in this 200 ppm water) but significantly less effective at higher concentrations. It is superior to LAS at all concentrations under .3%. Like most other non-phosphate compositions the 90-730 formulation looks comparatively better on cotton than on blend fabric.

Following up on the idea that mixtures of surfactants might be more effective than the single components two commercial liquid nonphosphate detergents consisting essentially of surfactants without builder were tested. Results are shown in Figures 17-20. These products, both of which contain in the neighborhood of 40% surfactant and include both anionic and nonionic surfactants, behaved remarkably alike. In the low concentration ranges, below .1 to .15%, they are superior to AATCCWOB. Above about .15% they are not quite equal to AATCCWOB, although on cotton fabric they are almost equal.

The only unbuilt surfactant that was bundle tested was the 90-730 formulation containing 27% active surfactant. This was tested against AATCCWOB at .15% in Rockville tap water. Both the panel ratings and the reflectometer readings showed the AATCCWOB significantly superior at the end of 6 cycles. At this low concentration, however, even the AATCCWOB did not get the laundry satisfactorily clean, and the test cannot therefore be considered satisfactory. No further launderability work, however, was done with the 90-730 surfactant. The sample at hand had caused more yellowing than the control in all the tests. Properties other than launderability are shown in the appropriate tables.

The soap and soap-LSD formulations were examined for effect on the fabric. Data in Table 13 show that the ash content increases considerably more and the alcohol extractable content much more with these detergents than with AATCCWOB. The LSD helps to keep the ash content down to a reasonable level, but has less effect on the alcohol extractable content.

B. FORMULATIONS BUILT WITH CARBONATE AND/OR SILICATE

Early in the course of the project interest in carbonate as a builder was very high. This was largely a result of the introduction into the retail market by Sears Roebuck of a detergent containing approximately 10% of a fatty alcohol ethoxylate surfactant and 65% sodium carbonate. A relatively small number of high carbonate formulations were accordingly prepared and examined for launderability with results shown in Table 6. These data indicate that certain nonionic surfactants and some surfactant mixtures provide reasonably good laundering performance in high carbonate formulations, provided a sufficient percentage of surfactant is present. Later in the program two commercial detergents, one containing about 20% carbonate and the other free of carbonate but containing about 20% of silicate, were tested using Colgate soil. The results are shown in Figures 21-22. The fact that detergents of high carbonate content cause extensive ash build-up in the substrate fabric is evidenced in Table 13.

Data in Tables 1, 1a, 7 and 7a show that a high silicate content tends to improve launderability significantly, and the effect on the fabric (Table 13) is not too objectionable.

High carbonate apparently has no unfavorable effect on algal growth (item 8, Table 9), nor on acute aquatic toxicity (item 10, Table 10). It may pose a possible hazard problem with regard to esophageal irritation (Table 12).

C. FORMULATIONS BUILT WITH NTA (nitrilotriacetic acid)

In the early stages of the program, and within the soap and detergent industry even before regulatory action on phosphate was being considered, NTA was regarded as the most promising phosphate replacement. Accordingly a modicum of launderability testing was done to check the efficacy of this compound.

Table 3 shows that NTA is a powerful builder for all the classes of surfactant which were tested. It is particularly effective with the alpha olefin sulfonates (Items 3 and 7) giving negative delta G values on all four fabric-soil combinations. One of the big questions with regard to NTA, aside from the question of its possible hazard in use, was whether it could be made into a detergent of acceptable physical form. It was found, as shown in Table 8, that the combination of NTA with alpha olefin sulfonate formed a dry powder of good physical characteristics.

This formulation (Item 7 of Table 3) was examined for laundering performance over a range of water hardnesses and at concentrations ranging from .1 to .3%. The results are shown in Table 3-A. It is evident that this formulation is a rasonably good match for the standard phosphate detergent over the whole range of use conditions. It is significantly inferior only on sebum soiled blend fabric at low concentrations in hard water. When enough detergent is used to soften the water the performance again matches that of the phosphate standard. In this connection it should be borne in mind that this formulation contains 30% NTA as against 40% tripolyphosphate in the standard detergent.

Acute aquatic toxicity tests on NTA showed it to have no adverse effects on the test organisms even at 500 ppm (Table 10, item 23). BOD tests (data not shown) indicated that NTA is not as rapidly biodegraded as LAS or some of the other proposed phosphate replacements such as citrate.

D. SAND FORMULATIONS

SAND is the abbreviation for the disodium salt of the monoamido derivative of nitrilotriacetic acid. This material was offered for testing relatively early in the program. The supplier, on the basis of his own laboratory work was convinced that this material strongly resisted hydrolysis and therefore could not be considered simply as a reservoir or source for NTA. On this basis the compound was tested for launderability and other properties. Launderability data on the more important SAND formulations are shown in Table 4. SAND, like NTA, is a good builder for all types of surfactants but appears less effective on LAS and on the alkane sulfonate type of surfactant than might be desired. It is exceptionally effective with some of the ether carboxylate surfactants (Item 6) and also with the fatty alcohol ethoxylates.

Table 8 shows that SAND is a very desirable constitutent of dry mixes, being one of the very few materials that appears to form a satisfactory dry mix with the fatty alcohol ethoxylates as well as with other surfactants that are normally easier to dry.

As shown in Table 10, item 25, SAND has no significant effect on the test organisms used in the aquatic toxicity tests. Biodegradability tests (data not shown) indicated about the same degree of resistance to aerobic biodegradation as shown by NTA.

E. SHIM (HEIDA) FORMULATIONS

SHIM, later abbreviated HEIDA by the supplier, was submitted for study early in the program. It is the disodium salt of beta hydroxyethyl iminodiacetic acid.

Referring to Table 5, SHIM, like SAND, is a good builder for all types of surfactants although it is less effective on LAS than on the others. Comparing Items 1 and 2 it appears that 30% SHIM in a formulation is sufficient when the formulation is used at the .3% level in 200 ppm water. In our essentially limited work on physical forms we found that SHIM compositions failed to give good drum dried products. It did prove possible, however, as shown in Table 8-A, to make stable liquid formulations containing SHIM as a builder. A hydrotrope was necessary, sodium octenyl succinate being best for the nonionic, and sodium xylene sulfonate being best for the anionics. The essential antiredeposition agent NaCMC would not dissolve in any of these compositions, but it can presumably be suspended satisfactorily as it is in present day commercial heavy duty liquids.

When used as a builder for LAS at the 30% level SHIM showed excellent performance in the Colgate soil test (Figures 23-24). At a concentration level of .2% or higher, where sufficient SHIM is present to overcome all the water hardness, the absolute level of soil removal is equal to that of the control high-phosphate detergent, even on blend fabric.

Two different SHIM formulations were bundle tested. The first was a 20/8/1/30/41 formulation in which the surfactant was alpha olefin sulfonate code 22-155. This was tested at 0.2% concentration in Rockville tap water against the AHAM detergent (cf. Appendix B). At the end of six cycles the panel rated AHAM superior by a score of 9.75 to 6.25. This difference was later shown to be due to a larger residue of the original mill-finish fluorescent whitening agent in the AHAM washed fabrics than in the SHIM washed fabrics. The former appeared slightly whiter to the eye in daylight even though the soil content was not lower. Instrumental readings on the pillowslips of both blend and cotton fabrics showed no significant difference between the test and the control formulations. The second bundle test was performed on a 20/8/1/30/41 formulation in which the surfactant was LAS. This was tested at 0.3% in tap water against AATCCWOB. In this test the panel gave the SHIM formulation the non-significant numerical edge 9.65 to 9.35. Instrumental measurements of reflectance were made on all the laundered items (not only on the pillowslips). Statistical analysis as well as eyeball judgment of the data showed no significant difference between the two detergents. At this ample concentration both bundles of laundry were satisfactorily clean from the consumers' point of view.

SHIM proved to be fully satisfactory with regard to biodegradability (Table 11) acute aquatic toxicity (Table 10) and algal stimulation (Table 9). Hazard tests were run on a 25% aqueous solution of the unformulated material (item 56-445 in Table 12) and on two finished formulations 65-1 and 65-2 containing respectively 18% and 25% of 100% active SHIM. The results (Table 12) suggest that SHIM is close to the borderline with regard to both oral and dermal toxicity, and that the toxicity of a composition containing SHIM may depend to a great extent on the character of the accompanying surfactant. It should be noted that these data are quite limited, and that much more extensive testing is needed before judging the degree of hazard which SHIM presents.

F. FORMULATIONS BASED ON POLYMERIC BUILDERS

The launderability data in Table 6 which were developed early in the program show that the polymeric builders vary quite widely in their effect, and even those which are effective with one type of surfactant may be quite unsatisfactory with another. Several of the materials in this table, notably the builder coded 40-310, are described in the patent literature as being quite effective. It is unfortunately quite resistant to biodegradation under ordinary circumstances. None of the materials shown in this table has been satisfactorily biodegradable. There are of course many polymers, such as the proteins and some of the carbohydrates, that are readily biodegradable, and there is no reason why a combination that exhibits good biodegradability together with good building power should not exist. A continuing effort was made throughout the course of the project to discover polymeric builders that were biodegradable. Preliminary launderability tests (made prior to or simultaneously with biodegradability tests) are shown in Table 6a. The polyacrylic acid builders were studied more extensively than any other class for the following reasons: first, they had a more favorable economic picture than most of the other materials; second, they were available in a wide range of molecular weights; third, they were known to be toxicologically harmless and non-stimulating to the growth of algae. The philosophy was that monomeric acrylic acid is biodegradable but not a builder; acrylic polymer of high molecular weight is a good builder but is not biodegradable. Somewhere in between we must come to a molecular weight range where the material has both biodegradability and building power or has neither. The series of acrylic polymers 92-745, 100-823 and 100-824 graded in average molecular weight from about 3000 to well under 1000 were studied on this basis. The chelation curves in Figure 49 show that the lower molecular weight material has considerably lowered sequestering power, but still might have a satisfactory building effect. Figures 25 and 26 show the detersive effect of Calnox 214 DN a polyacrylic acid with a stated mean molecular weight of 750. It performed remarkably well on cotton on this test, and even on blend fabric it was fully satisfactory in the LAS formulation, at 0.3% concentration. This material has low aquatic toxicity. It is at least partially biodegradable, although the action is slow.

A polymeric builder that has been extensively explored and reported upon by the producer is the hydroxylated acrylic identified as POCNa (code 104-860). The sequestration curve on this material (Figure 48) indicates that a high proportion would have to be used in a detergent formulation to produce a satisfactory building effect. Figures 27-28 show that in an LAS formulation at 50% active content it performed well in the concentration range about 0.2%, especially on blend fabric. This material was made up with LAS to a 20/8/1/50/21 formulation, and was bundle tested against AATCCWOB at 0.3% in tap water. After 6 cycles both bundles were satisfactorily clean. The panel rated the control detergent 10.9 against 9.1 for the POCNa formulation, an insignificant difference. Instrumental reflectance readings were made on all laundered items. They showed no significant difference between the two detergents. The biodegradation was faster and more extensive than that of any other polymeric builder tested (Table 11). The aquatic toxicity, like that of all other polymers tested, was low.

Homopolymers and copolymers of maleic acid have long been known to have remarkably good building powers, but to be quite resistant to biodegradation. A recent patent application (Netherlands Application 7205685 to Shell International Research) describes certain low molecular weight telomers of maleic acid which are stated to be biodegradable. A telomer of this type was prepared, following the patent example closely, using isopropyl acetate as the telogen. The product was purifed thoroughly and characterized by the usual tests, and given the code designation 106-866. The chelation curve (Figure 46) showed it to be an exceptionally powerful and efficient sequestrant. Detergency data are shown in Table 6a, items 37-40, and in Figures 29-32. When used in equal quantities it appears fully equal to sodium tripolyphosphate as a builder for LAS in these testing regimens.

Due to termination of the program this material was not bundle tested. It performed well in the aquatic toxicity test. In the BOD test it showed moderately extensive and rapid oxygen absorption, in contrast to a maleic homopolymer which showed no oxygen absorption whatsoever. However, the molecular weight is such that the isopropyl acetate telogen moiety could have accounted for a large part of the oxygen take-up. At this stage of the investigation therefore the biodegradability of this particular example of the products described in Netherlands Application 7205685 must be regarded as questionable (Table 11).

Two other polymeric materials gave indications of being at least partly biodegradable. One of these, coded 102-834, is stated to be a starch derivative. Its chelation curve is shown in Figure 48, and its detergency performance in Table 6a, items 51 and 52. The other material coded 100-821 was not identified by the supplier. The detergency screening data (Table 6a, items 60-63) were not especially promising.

G. FORMULATIONS BASED ON NON-NITROGENOUS MONOMERIC BUILDERS

Data on the more important monomeric builders tested in the earlier stages of the program are shown in Table 7. Diglycollic acid (coded 38-279) showed moderate promise as a detergency builder, and was biodegradable (Table 11). The supplier, however, indicated that it posed a toxicity problem so it was not studied further. Item 13, mellitic acid (coded 74-606) is one of a group of similar compounds described as builders in a series of recent patents. Although promising, this compound was not studied further because of poor availability. Item 15, the furan derivative coded 76-620, had good building action but failed the biodegradability test (Table 11).

Of the other materials, citric acid was studied most extensively. As is evident from the data it has proved to be particularly effective when used with about 20% of a high ratio silicate. Under our conditions of concentration and water hardness a minimum of about 30% citrate appears to be necessary to get maximum effect. This is evidenced abundantly in the table. The silicate citrate combination is most effective with the fatty alcohol ethoxylate nonionics (Item 22), certain ether carboxylates (Item 31), and the sulfo zwitterionics (Items 35 and 36). The latter formulations dry very well as shown in Table 8, and the nonionic formulation can be made into a satisfactory liquid as shown in Table 8-A.

Later in the program the builder carboxymethyl oxysuccinate (CMOS coded 96-789) was studied extensively. The screening data shown in Table 7a indicate that it is a builder for both anionic and nonionic surfactant types. It also proved to be biodegradable, nontoxic to aquatic organisms and without effect on algal growth. Further data on CMOS built compositions are shown in Figures 11-12 and 33-34. When used at the 30% level with LAS, full effectiveness of the detergent is reached at .3% concentration.

A 20/8/1/30/41 formulation of LAS and CMOS was bundle tested against AATCCWOB at two different concentrations, .15% and .3%. At .15% the panel preferred AATCCWOB by a margin of 14 to 5, a significant difference supported by the reflectance readings. At .3% the CMOS was preferred by a score of 10.65 to 7.35, a non-significant difference also supported by the reflectance data.

Several citrate compositions were tested extensively, based on the promising results of the screening tests shown in Table 7. These were based on surfactants other than LAS. Three of these compositions were solids, all containing 30% sodium citrate and 20% silicate and having the proportions 20/20/1/30/29. Formulation 64-1 used an ether carboxylate surfactant coded 60-486. Formulation 64-2 used a sulfozwitterionic surfactant coded 54-433, and Formulation 67-1 another sulfozwitterionic coded 42-348. A liquid composition, listed as item #1 in Table 8a, was also prepared for further testing.

Formulations 64-1 and 64-2 were tested against the two control detergents at various concentrations and water hardnesses. All five test procedures (soils) as outlined in Appendix B were used. For quick reference the procedures are: #1 Empa soil single cycle; #2 Colgate soil single cycle; #3 Spangler soil multicycle; #4 Vacuum cleaner dry soil multicycle; #5 Vacuum cleaner sebum or oily soil multicycle. The results are shown in Tables 7b and 7c. These formulations 64-1 and 64-2 were bundle tested against the AHAM detergent at .2% concentration in Rockville tap water. The panels rated 64-1 equal to the control detergent, but 64-2 was rated inferior, largely due to a slight yellowing effect. Details of these tests are given in Appendix B.

Formulation 64-1 was chosen for one of the two chronic aquatic toxicity studies made during the course of the program. The other study was made on the representative high-phosphate detergent AATCCWOB. Both studies are reported together as Appendix E. The 64-1 formulation appears to be no more harmful to aquatic life than the high-phosphate material.

H. WASHING WITH ION EXCHANGE RESINS

Data on the ion exchange resin washing experiments outlined in the previous section of this report are presented qualitatively rather than in tabular form.

When given adequate time to soften the water the resins both performed very well, enabling the unbuilt formulations to wash as well as in distilled water and as well as the corresponding phosphate-built detergents in hard water. The Dowex was quite slow, requiring almost an hour to soften the water and effect the washing. The Amberlite was more rapid in its action requiring only 30 minutes to produce the full effect. Further tests using multicycle procedures on vacuum cleaner soils gave essentially similar results. The ion exchange resin facilitated soil removal but required considerable time to exert its effect.

It is evident that a cation exchanger which worked more rapidly than the two that were tried could probably provide a practical washing system. Faster acting resins might be made by increasing the bead porosity and decreasing its dimension, by making the resin in fibrous form, etc. The manner in which the resin is deployed in the bath could also be altered to increase the rate of Ca^{++} removal. Circulation of the wash liquor through a bag of beads is obviously not optimal.

DISCUSSION

The various possibilities for developing satisfactory phosphate-free detergent formulations are conveniently discussed according to the classification scheme used in the previous section, i.e. eight different composition categories and seven different categories of performance or properties.

A. UNBUILT SURFACTANTS

The data indicate that synergy among two or more surfactants with regard to soil removing power is a very real thing. A formulation containing in the range of 40% total surfactant and no significant quantity of builder appears able to perform reasonably well at practical concentrations, provided the surfactant mixture is suitably chosen. Possibly the best evidence of this is provided by the commercial detergents D (Code 104-855) and E (code 96-782). Added evidence is provided by the laboratory performance of the commercial detergent extract coded 32-237.

Single surfactants such as LAS, FAEN or the experimental D-116 (code 90-730) appear less effective than the mixtures, although limited work with the sulfonated zwitterionics indicates that they might prove sufficiently effective. They are at present costly, however, and more a specialty than a bulk item.

The soap-LSD combinations fall into a special category. To give effective soil removal in hard water a high concentration is needed, which makes the economics seem unattractive. Furthermore, as shown in Table 13, althcugh the LSD does lower the amount of undesirable residue left on the fabric it does not lower it to the level expected by consumers accustomed to phosphate containing detergents. It should be noted that the soil removing power of these materials is very high when used in sufficient concentration.

B. CARBONATE-SILICATE FORMULATIONS

A high carbonate content certainly increases the soil removal power of certain surfactants and surfactant mixtures. It is objectionable, however, in causing rapid build up of solid residues on the fabric when used in hard water. A relatively low carbonate content, in the range of 20%, is correspondingly less objectionable but may not contribute enough extra washing power to be worthwhile (cf Figures 21 and 22).

The high ratio silicates appear to have some building power for certain surfactants but not for others. They also appear to be synergistic with certain other builders, notably citrate as discussed below. Silicates do not appear to have anywhere near the adverse effects on fabric that carbonate has and are unobjectionable in other respects as long as the ratio of silica to soda is in the range of 2:1 or higher. Evidence of their effectiveness in appropriate formulations is provided by commercial detergent C (coded 96-783) in which silicate appears to be the only builder present in significant quantity.

C. NTA FORMULATIONS

The present studies have confirmed the virtues of NTA, as evidenced by all the data. It is an excellent builder for all surfactants tested, including the large tonnage inexpensive surfactants now used in phosphate formulations. Investigation of some possible disadvantages of NTA, reported in the technical literature and to a certain extent publicized, has not been within the scope of this program.

D. SAND FORMULATIONS

To the extent that it has been tested SAND is a good builder of detergency, similar in this respect to NTA or phosphate.

The similarity in structure between SAND and NTA, and the fact that SAND can in theory be converted to NTA by a simple hydrolysis reaction, would make SAND subject to the objections that have been raised against NTA. It would presumably be necessary to prove that these objections were not valid in the case of SAND, a difficult and time-consuming task outside the scope of this program.

E. SHIM (HEIDA) FORMULATIONS

SHIM is an excellent builder for the detergency of all surfactants tested, in the same class as phosphate and NTA. It is readily biodegradable and fully satisfactory with regard to biostimulation and acute aquatic toxicity. SHIM is sufficiently different from NTA in chemical composition so that the objections raised against NTA could not legitimately be translated as applicable to SHIM. Its toxicity is close to the limits recommended by FDA and Consumer Products Safety Commission, and more extensive work would have to be done on SHIM formulations before they could be cleared in this regard. SHIM may also be difficult to formulate into a satisfactorily storable solid detergent although it can readily be formulated to liquids.

F. FORMULATIONS BASED ON POLYMERIC BUILDERS

None of the polymeric builders tested provide the rapid biodegradability characteristic of the "soft" surfactants and some of the monomeric builders. Several, notably the acrylics and maleics, have outstanding building action for the conventional tonnage surfactants. It seems to be the general rule, however, that building effect must be traded off against biodegradability. The best compromise in this regard that we have seen so far is the POCNa hydroxylated acrylic polymer (code 104-860). The formulation based on LAS surfactant and containing 50% of this builder gave satisfactory laundering performance at concentrations of 0.2% or higher. Two other polymeric builders show promise of simultaneously meeting both the launderability and biodegradability requirements. These are the very low molecular weight acrylic (code 100-823) and the maleic telomer (code 106-866). Considerably more work would be required on both these products, however, before a final judgment on their overall satisfaction could be rendered.

Polymeric builders in general appear to be biologically inert: non-toxic to aquatic life and non-stimulating to algal growth. This characteristic extends to their lack of biodegradability.

G. FORMULATIONS BASED ON NON-NITROGENOUS MONOMERIC BUILDERS

The two non-nitrogenous monomeric builders that appear as promising replacements for phosphate are citric acid and CMOS. Of these citric acid is by far the more thoroughly explored. The detergency building action of citrate varies considerably from surfactant to surfactant as might be expected of a relatively weak chelating agent (cf. Figure 47). Formulation 64-1 shows that with a suitable surfactant citrate can provide reasonably satisfactory launderability. It is highly probable that a synergistic mixture of surfactants could also be satisfactorily built with citrate. The only citrate built commercial detergent tested (Detergent O, coded 90-279, Figures 35-36) was a European product designed for European washing conditions. There is at least one widely used citrate built detergent in the phosphate-free market in the U.S.A. Citrate has the great advantage of being completely unobjectionable from the ecological and health hazard standpoints.

CMOS appears to have the same advantages as citrate, and to be somewhat stronger with regard to both sequestration (cf. Figure 47) and building action. It gives better results than citrate as a builder for LAS. Time did not permit complete testing of CMOS with regard to all the property categories, but on the basis of evidence at hand it must be regarded as a serious contender in the phosphate-substitute competition.

H. WASHING WITH ION EXCHANGE RESINS

From the environmental point of view a washing system based on ion exchange resins is close to ideal. No soluble builder goes down the drain. Since all acceptable builders are visualized as being biodegradable, any combination of surfactant and sequestering builder would increase the BOD load on the sewage disposal systems and/or the streams into which it flowed. In the ion exchange system the surfactant would be the only source of significant BOD. The only product which might seem to require special disposal is calcium chloride resulting from regeneration of the resin. However the calcium is simply that which was removed from the laundry's water supply, and the chloride is counterion to the sodium given up by the resin in the softening step. The only net addition to the watercourse in this process is the sodium chloride used in regenerating the resin.

Although we believe the ion-exchange resin system to be very promising other priorities in the program precluded its further exploration. Successful further development would most probably come from improvements in the resin, and the form and manner in which it is used. Such development would seem to be the province of researchers and manufacturers of cation exchange resins. Detergent manufacturers and formulators would also have to contribute, however, since compatibility with minor adjuvants of the formulation would have to be worked out. Similarly, much new data would have to be elaborated on the detersive power of various surfactants and surfactant mixtures in softened water. Finally, the various difficulties that are inevitably involved when introducing a new process to the consumer would have to be worked out. The projected ultimate advantages of the process might nevertheless be worth any introductory difficulties.

In deciding which of the formulations developed in this program and discussed above might be most promising it is of interest to see what the soap and detergent industry has introduced into the phosphate-free market since the start of the program. The first phosphate substitute was NTA, no longer being used in the U.S.A. because the hazard question has not (as of this writing) been definitely answered. Some high carbonate (more than 45%) formulations have been and are still being marketed. A considerable number of low carbonate (20-25%) formulations are being marketed, some of which contain about an equal amount of silicate. Some citrate formulations have appeared, including some in which the citrate is augmented by carbonate and/or silicate.

A final important group includes formulations consisting essentially of unbuilt surfactants or surfactants built only with silicate. To the writers' knowledge no polymer-built formulations have been introduced in significant quantity, nor have there appeared any formulations built with nitrogenous or non-nitrogenous monomeric builders other than citrate. There also seems to have been little increase in the use of soap or soap-based compositions for heavy duty household laundering in the phosphate-free jurisdictions. It is of little profit to speculate on the reasons for this situation. There is no doubt that costs play an important role. The leading surfactants are themselves relatively inexpensive. If 50 parts of surfactant alone will do as good a job as 20 parts surfactant plus 30 parts builder, then the builder must be less costly than the surfactant to justify its use. Provided that performance is adequate the choice among formulations, whether they consist of surfactants alone or surfactant-builder combinations, depends largely on overall cost efficiency. Other economic and technical factors, however, also enter into consideration.

During the three year course of this program the rate at which patents have been issued on phosphate-free detergent compositions has increased greatly; and at the present writing it has not started to diminish. Perusal of these patents, both U.S.A. and foreign, has been of obvious value in conducting this program, and in some instances (e.g. POCNa and the maleic telomer) has led to some very promising formulations which might otherwise never have been made or tested. A selected list of recent patents, classifed according to the outline used in this report, is included as Appendix D. In almost all citations the Chemical Abstracts (CA) reference as well as the patent number is given to facilitate retrieval.

Table 1. DETERGENCY OF SURFACTANTS WITHOUT BUILDER, .3%, 4 washes, 200 ppm water

					Delta G Values			
					Vacuum Soil		Sebum Soil	
Item No.	Surfactant Code No.	Surfactant Type	Proportions[k]	Series Ref. No.	Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
1	68-127	Fatty Alcohol Ethoxylate Nonionic	12/8/1/0/79	--[a]	4.5	2.5	4.2	2.0
1a	68-127	" " " "	"	--[a]	2.1	1.1	2.4	1.6
1b	68-127	" " " "	"	--[a]	6.2	4.3	5.4	3.2
2	68-127	" " " "	12/8N/1/0/79	149-50	5.3	2.1	5.4	2.3
3	68-127	" " " "	12/8D/1/0/79	122,147	7.2	4.5	6.3	4.5
4	68-127	" " " "	25/8/1/0/66	--[b]	3.8	1.7	1.9	-.2
5	68-127	" " " "	20/8/1/0/71	--[c]	5.0	2.2	2.6	1.1
6	68-127	" " " "	20/8GD/1/0/71	92-3	6.7	2.8	5.1	1.6
7	68-127	" " " "	20/25/1/0/54	92-3	4.7	1.6	3.5	-.2
8	68-127	" " " "	20/25GD/1/0/54	92-3	7.4	3.1	3.6	.5
9	68-127	" " " "	20/8D/1/0/71	122,147	7.2	4.7	3.4	3.2
10	68-127	" " " "	12/20GD/1/0/67	102-3	10.1	8.9	6.9	5.6
11	51-104	" " " "	25/8/1/0/66	14	4.1	-1.2		
12	20-138	" " " "	25/8/1/0/66	--[d]	6.0	-.5		
13	68-134	" " " "	25/8/1/0/66	21-2	4.5	2.7	-.5	.7
14	68-134	" " " "	12/8/1/0/79	23-4	7.4	2.5	3.1	1.2
15	51-93	" " " "	25/8/1/0/66	13	3.5	.1		
16	43-67	" " " "	25/8/1/0/66	7		1.4		

(Continued)

Table 1 (Continued)

Item No.	Surfactant Code No.	Surfactant Type	Proportions[k]	Series Ref. No.	Delta G Values Vacuum Soil Blend Fabric	 Cotton Fabric	 Sebum Soil Blend Fabric	 Cotton Fabric
17	51-100	Fatty Alcohol Ethoxylate Nonionic	25/8/1/0/66	14	9.0	.3		
18	51-101	" " " "	25/8/1/0/66	14	6.9	-.5		
19	51-105	" " " "	15/8/1/0/76	132-3	3.8	1.2	7.4	5.9
20	51-105	" " " "	25/8/1/0/66	132-3	3.9	.6	4.3	3.9
21	51-105	" " " "	40/8/1/0/66	132-3	4.0	1.0	2.7	2.2
22	31-230	Hydroxylated Nonionic	25/8/1/0/66	87-8	10.1	5.0	9.6	3.1
23	26-191	" "	25/8/1/0/66	23-4	10.0	5.8	5.6	2.7
24	26-189	" "	25/8/1/0/66	23-4	4.1	1.7	6.1	3.3
25	43-83	" "	25/8/1/0/66	23-4	2.4	1.2	1.2	.7
26	43-83	" "	25/50/1/0/24	23-4	1.6	.7	2.5	1.3
27	20-144	" "	25/8/1/0/66	11	6.0	2.0		
28	20-145	" "	25/8/1/0/66	5		4.2		
29	48-374	Amine Oxide	25/8/1/0/66	84-5	8.9	5.1	9.9	3.8
30	51-91	Alkane Sulfonate Anionic	25/8/1/0/66	10		3.5		
31	22-155	Alpha Olefin Sulfonate Anionic	20/8/1/0/71	--[e]	7.4	4.7	7.5	2.8
32	22-155	" " "	20/20/1/0/59	--[f]	5.0	3.2	5.8	2.4
33	74-604	" " "	20/8/1/0/71	145-6	9.1	4.6	8.3	4.2
34	74-604	" " "	20/20/1/0/59	145-6	9.0	5.0	6.7	3.1
35	68-558	" " "	20/8/1/0/71	124-5	4.5	4.3	3.5	2.1

(Continued)

Table 1 (Continued)

Item No.	Surfactant Code No.	Surfactant Type	Proportions[k]	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
36	58-471	Ether Sulfate Anionic	12/8/1/0/79	106-7	4.8	3.6	2.7	.5
37	62-491	" " "	12/8/1/0/79	104-5	3.9	1.9	3.5	1.6
38	62-491	" " "	20/8/1/0/71	104-5	4.1	2.2	4.0	1.6
39	62-491	" " "	12/20/1/0/67	102-3	6.4	5.2	7.8	3.6
40	62-491	" " "	12/20GD/1/0/67	102-3	9.2	4.2	9.0	6.4
41	62-492	" " "	12/8/1/0/79	104-5	4.0	1.6	4.8	1.6
42	62-492	" " "	20/8/1/0/71	104-5	3.9	1.8	4.3	1.1
43	40-332	Ether Carboxylate Anionic	12/8/1/0/79	62-3	6.7	1.9	8.1	1.9
44	40-332	" " "	25/8/1/0/66	62-3	4.6	2.1	3.7	-.6
45	60-486	" " "	12/8/1/0/79	106-7	2.8	1.2	6.4	.5
46	60-486	" " "	12/20/1/0/79	102-3	7.8	6.2	10.0	4.9
47	60-486	" " "	12/20GD/1/0/79	102-3	7.0	5.5	8.0	3.9
48	60-486	" " "	20/20/1/0/59	128-9	1.5	.6	2.8	-.1
49	68-109	Sulfonate Ampholytic	25/8/1/0/66	15	4.1	1.7		
50	68-108	" "	25/8/1/0/66	87-8	5.5	2.4	12.3	3.5
51	46-357	Carboxy Betaine Zwitterionic	25/8/1/0/66	84-5	3.3	1.7	3.9	.8
52	42-348	Sulfo Betaine Zwitterionic	25/8/1/0/66	84-5	1.4	-.2	4.4	-.2
53	42-348	" " "	20/20/1/0/59	__[8]	3.2	.8	3.5	1.4
54	54-431	" " "	25/8/1/0/66	87-8	4.5	2.1	5.3	.6

(Continued)

Table 1 (Continued)

Item No.	Surfactant Code No.	Surfactant Type	Proportions^{k}	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
55	54-433	Sulfo Betaine Zwitterionic	25/8/1/0/66	87-8	.9	-.4	3.9	-.3
56	54-433	" " "	20/20/1/0/59	130-1	1.6	2.9	5.5	2.1
57	32-237	Commercial Detergent Extract^{h}	25/8/1/0/66	28-9	4.1	.9	1.7	-.6
58	32-237	" " "	25/50/1/0/24	28-9	2.9	-.1	.9	-.4
59	32-237	" " "	25/8/3/0/64	28-9	2.9	.7	1.3	-.1
60	34-249	Linear Alkylaryl Sulfonate (LAS)	25/8/1/0/66	--^{i}	8.2	4.4	7.0	4.7
61	34-249	" " " "	20/8/1/0/71	--^{j}	7.8	4.5	6.8	4.7
62	34-249	" " " "	20/8GD/1/0/71	92-3	8.8	4.4	7.3	3.8
63	34-249	" " " "	20/25/1/0/54	92-3	6.0	3.7	4.9	2.9
64	34-249	" " " "	20/25GD/1/0/54	92-3	7.3	4.7	6.2	3.2
65	34-249	" " " "	20/20/1/0/59	94-5	10.7	5.4	7.0	5.1
66	34-249	" " " "	20/20GD/1/0/59	94-5	10.1	4.2	6.3	5.0
67	38-282	Commercial Detergent, Approx. 70 nonionic, 20 amine soap	as is	62-3	6.4	5.4	6.8	5.2
68	70-560	Commercial Detergent, Approx. 20 nonionic, 7 soap	as is	126-7	2.4	6.1	2.2	4.5
69	20-146	Mixture 85 low titer soap, 15 silicate D	as is	142-3	.1	-.3	0	.3
70	74-594	Mixture soap, lime-dispersing anionic, silicate ER 544-151A	as is	142-3	-.2	-1.3	-.6	-1.6

a = avg. of 14; b = avg. of 4; c = avg. of 5; d = avg. series 2, 4, 6, 11, 13, 14; e = avg. of 7; f = avg. of 3; g = avg. of 2; h = alcohol extract of a leading commercial detergent; i = avg. of 9; j = avg. of 3.
k = % surfactant/ % silicate/ % NaCMC/ % builder/ % sodium sulfate.

TABLE 1A. DETERGENCY OF SURFACTANTS WITHOUT BUILDER
.3%, SPANGLER SOIL, 3 WASHES, 200 PPM WATER

ITEM NO.	SURFACTANT CODE NO.	SURFACTANT TYPE	PROPORTIONS	SERIES REF.NO.	DELTA W BLEND FABRIC	DELTA W COTTON FABRIC
71	90-730	ANIONIC SULFONATE	10/7/1/0/82	213	7.5	3.4
72	90-730	ANIONIC SULFONATE	15/7/1/0/73	213	5.8	1.3
73	90-730	ANIONIC SULFONATE	27/8/1/0/64	231, 234, 239	5.0	1.6
74	68-127	FATTY ALCOHOL ETHOXYLATE NONIONIC (FAEN)	12/8/1/0/79	215, 233, 235, 238 244, 245, 249, 251	10.4	7.7
75	68-127	FAEN	12/20/1/0/67	238	10.4	5.0
76	68-127	FAEN	27/8/1/0/64	234	6.9	3.4
77	20-145	HYDROXYLATED NONIONIC	20/8/1/0/71	211	14.7	8.5
78	20-145	HYDROXYLATED NONIONIC	20/20/1/0/59	211	17.4	6.4
79	102-836	FATTY ACID DIETHANOLAMINE CONDENSATE + FAEN	15+5/8/1/0/71	246	5.0	0.3
80	102-836	FATTY ACID DIETHANOLAMINE CONDENSATE + FAEN	15+5/20/1/0/59	246	3.6	-1.4
81	34-249	LAS	20/8/1/0/71	236, 244, 245, 249 251	6.9	3.8
82	34-249	LAS	25/8/1/0/66	214, 224, 237	4.0	2.2

TABLE 1A. (CONTINUED)

ITEM NO.	SURFACTANT CODE NO.	SURFACTANT TYPE	PROPORTIONS	SERIES REF.NO.	DELTA W	
					BLEND FABRIC	COTTON FABRIC
83	34-249	LAS	25/20/1/0/54	237	3.6	0.6
84	34-249	LAS	27/8/1/0/64	234, 239	4.9	2.2
85	86-706	SOAP-LIME SOAP DISPERSER ER AF569-144-1	AS IS	216	-0.5	-0.1
86	86-707	SOAP-LIME SOAP DISPERSER ER AF569-144-2	AS IS	216	-0.4	-2.2
87	86-708	SOAP-LIME SOAP DISPERSER ER AF569-144-3	AS IS	216	-0.1	-1.7

Table 2. DETERGENCY OF SURFACTANT - CARBONATE FORMULATIONS, .3%, 4 washes, 200 ppm water

Item No.	Surfactant Code No.	Surfactant Type	Proportions	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
1	68-134	Fatty Alcohol Ethoxylate Nonionic	25/8/1/66/0	23-4	8.3	1.7	.9	.1
2	68-134	" " " "	12/8/1/66/13	23-4	5.2	.8	1.6	.5
3	51-93	" " " "	25/8/1/66/0	19-20	.7	1.1	1.3	-.6
4	51-101	" " " "	25/8/1/66/0	19-20	.3	1.5	.5	-.6
5	51-105	" " " "	25/8/1/66/0	19-20	1.6	.9	1.3	-.5
6	68-127	" " " "	25/8/1/66/0	23-4	1.7	-.8	0	0
7	68-127	" " " "	12/8/1/66/13	--[a]	3.5	.5	2.8	1.8
8	26-191	Hydroxylated Nonionic	25/8/1/66/0	23-4	3.6	1.0	1.3	1.2
9	26-189	" "	25/8/1/66/0	23-4	-.7	-.2	1.8	2.7
10	43-83	" "	25/8/1/66/0	23-4	2.6	-.8	2.7	.7
11	32-237	Commercial Detergent Extract[b]	25/8/1/66/0	28-9	1.2	-.2	.4	-1.1
12	34-249	Linear Alkylaryl Sulfonate (LAS)	20/8/1/35/36	120-1	4.5	4.9	4.3	3.9
13	34-249	" " " "	25/8/1/60/6	134			3.5	3.4
14	51-105	Fatty Alcohol Ethoxylate	12/8/2/66/12	30-2	4.3	-.1	5.3	1.0
15	51-105	" " "	12/20/2/66	30-2	.5	-2.3	4.7	1.3
16	36-278	Low Titer Soap, Nonionic Mixture	20/15/8/1/36/20	42-3	1.8	1.1	4.8	1.2
17	36-277	" " " " "	40/15/8/1/36/0	42-3	2.0	.3	3.8	.4
18	36-276	High " " " "	40/15/8/1/36/0	42-3	.1	-.1	.3	.8

a = avg. of 3; b = alcohol extract of a leading commercial detergent.

Table 3. DETERGENCY OF SURFACTANT - NTA FORMULATIONS, .3%, 4 washes, 200 ppm water

Item No.	Surfactant Code No.	Surfactant Type	Proportions	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
1	51-91	Alkane Sulfonate Anionic	20/8/1/30/41	100-1	1.1	1.0	.8	.6
2	34-249	Alkylaryl Sulfonate Anionic (LAS)	20/8/1/30/41	--[a]	.7	1.2	.7	.7
3	68-558	Alpha Olefin Sulfonate Anionic	20/8/1/30/41	124-5	-1.7	-.6	-1.8	-1.2
4	68-109	Sulfonate Ampholytic	25/8/1/30/36	21-2	.2	-.1	.2	1.1
5	68-134	Fatty Alcohol Ethoxylate Nonionic	25/8/1/30/36	21-2	2.0	.1	-1.2	.8
6	68-127	" " " "	12/8/1/30/49	72-3	-.3	.9	1.7	.1
7	22-155	Alpha Olefin Sulfonate	20/8/1/30/41	--[a]	-1.5	-.9	-.9	-1.7
8	20-138	Fatty Alcohol Ethoxylate Nonionic	25/8/1/30/36	--[a]	-2.5	-4.0		
9	51-93	" " " "	25/8/1/30/36	--[a]	-3.2	-1.9	1.5	.6

a = avg. of 3.

Table 3a. DETERGENCY OF NTA - ALPHA OLEFIN SULFONATE FORMULATION AT VARYING WATER HARDNESS AND CONCENTRATION[a]

Water Hardness ppm	Formulation Concentration percent	Soil - Vacuum Fabric - Blend Delta G	Soil - Vacuum Fabric - Cotton Delta G	Soil - Sebum Fabric - Blend Delta G	Soil - Sebum Fabric - Cotton Delta G
50	.10	-.5	.1	-.1	.8
50	.15	-.5	-.2	-.4	-1.2
50	.20	-1.7	-.8	-.3	-.8
50	.30	-1.6	-.3	.2	-.2
125	.10	.6	.9	3.0	1.8
125	.15	-.1	-.7	.9	-.2
125	.20	-.1	-1.0	.3	-.4
125	.30	-.6	-1.0	-.6	-.6
200	.10	.4	1.3	7.0	4.0
200	.15	-1.0	.7	3.6	1.4
200	.20	.6	.6	.4	-.4
200	.30	-1.9	-.5	-.6	-1.2
300	.10	.8	.5	3.7	.8
300	.15	.3	.7	4.9	1.1
300	.20	-3.3	-3.4	.9	.2
300	.30	-.2	-.2	-.8	0

a = Alpha Olefin Sulfonate Code 22-155, Formulation proportion 20/8/1/30/41

Table 4. DETERGENCY OF SURFACTANT - SAND FORMULATIONS, .3%, 4 washes, 200 ppm water

Item No.	Surfactant Code No.	Surfactant Type	Proportions	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
1	68-127	Fatty Alcohol Ethoxylate Nonionic	12/8/1/30/49	52-3	.2	-.5	.9	.6
2	68-127	" " " "	20/8/1/30/41	117-8	-1.4	-1.2	-1.0	-4.1
3	68-127	" " " "	12/8/1/50/29	--[a]	.5	-.3	.5	.3
4	62-491	Ether Sulfate Anionic	20/8/1/30/41	117-8	-.3	-.2	-.7	-3.9
5	22-155	Alpha Olefin Sulfonate Anionic	20/8/1/30/41	--[b]	-.3	-.5	.3	-1.5
6	60-486	Ether Carboxylate Anionic	20/8/1/30/41	117-8	-2.0	-2.3	-2.4	-5.1
7	51-91	Alkane Sulfonate Anionic	20/8/1/30/41	117-8	2.2	.8	1.4	-1.7
8	34-249	LAS Anionic	20/8/1/30/41	--[c]	3.9	2.2	3.0	3.2

a = avg. of 2; b = avg. of 3; c = avg. of 4.

Table 5. DETERGENCY OF SURFACTANT - SHIM FORMULATIONS, .3%, 4 washes, 200 ppm water

Item No.	Surfactant Code No.	Surfactant Type	Proportions	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
1	68-127	Fatty Alcohol Ethoxylate Nonionic	12/8/1/30/49	--[a]	.2	-.3	-1.4	-1.5
2	68-127	" " " "	12/8/1/50/29	89-90	.4	-1.3	-.7	.1
3	68-558	Alpha Olefin Sulfonate Anionic	20/8/1/30/41	124-5	.4	.3	-.6	-.9
4	22-155	" " " "	20/8/1/30/41	--[a]	-.2	.5	-.1	-.3
5	74-604	" " " "	20/8/1/30/41	145-6	.7	.6	1.2	0
6	60-486	Ether Carboxylate Anionic	12/8/1/30/49	106-7	-1.1	-.7	-1.5	-2.6
7	40-332	" " "	20/8/1/30/--[b]	155-6	-.7	-.9	0	-.9
8	78-634	" " "	20/8/1/30/--[b]	155-6	.8	.2	1.4	.4
9	78-633	" " "	20/8/1/30/--[b]	155-6	.4	.1	1.0	.6
10	78-635	Fatty Alkyl Sulfate Anionic	20/8/1/30/--[b]	155-6	-.3	0	.6	.8
11	58-471	Ether Sulfate Anionic	12/8/1/30/49	106-7	1.3	1.5	1.3	-.4
12	34-249	Alkylaryl Sulfonate Anionic (LAS)	20/8/1/30/41	98-9	1.6	2.4	1.6	1.0
13	34-249	" " " "	25/8/1/50/16	89-90	1.2	1.4	.6	1.2

a = avg. of 3; b = liquid formulation:water plus 10% hydrotrope.

Table 6. DETERGENCY OF POLYMERIC BUILDER - SURFACTANT FORMULATIONS, .3%, 4 washes, 200 ppm water

Item No.	Builder Type and Code	Surfactant Type and Code	Proportions	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
1	Acrylic 43-65	Sulfo Ampholytic 68-109	25/8/1/30/36	21-2	3.9	3.4	3.9	1.9
2	" "	Fatty Alcohol Ethoxylate Nonionic 68-134	25/8/1/30/36	21-2	3.7	2.3	-.4	.7
3	" 20-141	Sulfo Ampholytic 68-109	25/8/1/30/36	21-2	5.7	4.5	7.2	1.9
4	Maleic 40-310	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/30/49	52-3	-2.7	-2.1	-2.1	-1.1
5	" "	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/3/76	77-8	1.4	2.1	3.0	.3
6	" "	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/0/79	77-8	2.4	3.3	3.4	1.1
7	" "	LAS 34-249	25/8/1/30/36	52-3	-.4	-.5	0	.4
8	" "	" "	25/8/1/3/63	77-8	3.9	3.1	5.1	2.7
9	" "	" "	25/8/1/0/66	77-8	5.7	4.2	6.1	3.8
10	Carbohydrate 74-602	" "	25/8/1/50/16	147-8	3.9	2.5	2.1	2.3
11	Carbohydrate 74-602	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/30/49	147-8	4.1	2.6	3.6	1.9
12	Carbohydrate 66-530	Alpha Olefin Sulfonate 22-155	20/8/1/30/41	122-3	1.8	2.2	2.9	2.7

Table 6 (Continued)

Item No.	Builder Type and Code	Surfactant Type and Code	Proportions	Series Ref. No.	Delta G Values			
					Vacuum Soil		Sebum Soil	
					Blend Fabric	Cotton Fabric	Blend Fabric	Cotton Fabric
13	Copolymer 66-532	Fatty Alcohol Ethoxylate Nonionic 68-127	20/8/1/30/41	122-3	2.2	1.6	2.7	1.9
14	" "	Alpha Olefin Sulfonate 22-155	20/8/1/30/41	122-3	4.5	4.6	3.7	3.1
15	" "	LAS 34-249	20/8/1/30/41	122-3	5.7	4.1	5.3	5.0
16	" 66-533	Fatty Alcohol Ethoxylate Nonionic 68-127	20/8/1/30/41	122-3	-.2	-.4	-1.1	.4
17	" "	Alpha Olefin Sulfonate 22-155	20/8/1/30/41	122-3	1.0	.5	.8	1.5
18	" "	LAS 34-249	20/8/1/30/41	122-3	1.6	1.7	2.0	2.3
19	" 58-466	" "	20/8/1/30/41	98-9	2.0	1.3	2.2	2.1
20	" 58-467	" "	20/8/1/30/41	98-9	2.5	.7	1.6	2.3
21	" "	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/30/49	149-50	.9	-.6	1.6	-.6
22	" "	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8N/1/30/49	149-50	.7	-.2	-.2	-.4
23	" "	Alpha Olefin Sulfonate 22-155	20/8/1/30/41	151-2	.1	.1	.9	.1
24	" "	Alpha Olefin Sulfonate 22-155	20/8N/1/30/41	151-2	.3	.8	.4	.2

TABLE 6A. DETERGENCY OF POLYMERIC BUILDER-SURFACTANT FORMULATIONS
.3%, SPANGLER SOIL, 3 WASHES, 200PPM WATER

ITEM NO.	BUILDER TYPE AND CODE		SURFACTANT TYPE AND CODE		PROPORTIONS	SERIES REF. NO.	DELTA W	
							BLEND FABRIC	COTTON FABRIC
25	ACRYLIC	92-745	LAS	34-249	20/8/1/30/41	236	1.4	1.0
26	ACRYLIC	92-745	FAEN	68-127	12/8/1/30/49	215, 235	1.8	-1.4
27	ACRYLIC	100-823	LAS	34-249	20/8/1/30/41	244	3.3	1.5
28	ACRYLIC	100-823	LAS	34-249	20/8/1/50/21	245	1.6	0.1
29	ACRYLIC	100-823	FAEN	68-127	12/8/1/30/49	244	7.7	3.8
30	ACRYLIC	100-823	FAEN	68-127	12/8/1/50/29	245	2.5	1.7
31	ACRYLIC	100-824	LAS	34-249	20/8/1/30/41	244	2.9	1.2
32	ACRYLIC	100-824	FAEN	68-127	12/8/1/30/49	244	3.6	2.0
33	HYDROXYLATED ACRYLIC COPOLYMER	104-860	LAS	34-249	20/8/1/30/49	251	2.9	1.2
34	HYDROXYLATED ACRYLIC COPOLYMER	104-860	LAS	34-249	20/8/1/50/29	251	2.7	0.8
35	HYDROXYLATED ACRYLIC COPOLYMER	104-860	FAEN	68-127	12/8/1/30/49	251	7.5	7.7
36	HYDROXYLATED ACRYLIC COPOLYMER	104-860	FAEN	68-127	12/8/1/50/29	251	4.8	5.5

TABLE 6A. (CONTINUED)

ITEM NO.	BUILDER TYPE AND CODE		SURFACTANT TYPE AND CODE		PROPORTIONS	SERIES REF.NO.	DELTA W BLEND FABRIC	DELTA W COTTON FABRIC
37	MALEIC TELOMER	106-866	LAS	34-249	20/8/1/30/41	251	-0.3	-0.2
38	MALEIC TELOMER	106-866	LAS	34-249	20/8/1/50/21	251,267	-0.3	-0.6
39	MALEIC TELOMER	106-866	FAEN	68-127	12/8/1/30/49	251	0.5	0.3
40	MALEIC TELOMER	106-866	FAEN	68-127	12/8/1/50/29	251	-0.5	0.0
41	MALEIC HOMO-POLYMER	106-870	LAS	34-249	20/8/1/30/41	251	0.3	0.0
42	MALEIC HOMO-POLYMER	106-870	FAEN	68-127	12/8/1/30/49	251	0.4	-0.6
43	MALEIC COPOLYMER	86-709	LAS	34-249	25/8/1/30/36	214	1.3	-0.2
44	MALEIC COPOLYMER	86-709	FAEN	68-127	12/8/1/30/49	215	3.9	1.1
45	CARBOHYDRATE	86-704	LAS	34-249	25/8/1/30/36	214,224	4.7	1.0
46	CARBOHYDRATE	86-704	FAEN	68-127	12/8/1/30/49	215	9.8	6.0
47	CARBOHYDRATE	100-822	LAS	34-249	20/8/1/30/41	244,249	4.2	3.1
48	CARBOHYDRATE	100-822	LAS	34-249	20/8/1/50/21	245,249	1.6	-0.1

TABLE 6A. (CONTINUED)

ITEM NO.	BUILDER TYPE AND CODE		SURFACTANT TYPE AND CODE		PROPORTIONS	SERIES REF.NO.	DELTA W	
							BLEND FABRIC	COTTON FABRIC
49	CARBOHYDRATE	100-822	FAEN	68-127	12/8/1/30/49	244.249	4.6	3.9
50	CARBOHYDRATE	100-822	FAEN	68-127	12/8/1/50/29	245,249	3.1	3.5
51	CARBOHYDRATE	102-834	LAS	34-249	20/8/1/50/21	245	2.0	0.0
52	CARBOHYDRATE	102-834	FAEN	68-127	12/8/1/50/29	245	3.2	1.6
53	UNIDENTIFIED CARBOXYLATED POLYMER	86-705	LAS	34-249	25/8/1/30/36	214.224	1.7	0.5
54	UNIDENTIFIED CARBOXYLATED POLYMER	86-705	LAS	34-249	20/8/1/30/41	236	5.3	1.1
55	UNIDENTIFIED CARBOXYLATED POLYMER	86-705	FAEN	68-127	12/8/1/30/49	215.235	5.8	1.6
56	UNIDENTIFIED POLYMER	98-806	LAS	34-249	20/8/1/30/41	236	1.4	1.4
57	UNIDENTIFIED POLYMER	98-806	FAEN	68-127	12/8/1/30/49	235	5.8	1.2
58	UNIDENTIFIED POLYMER	98-807	LAS	34-249	20/8/1/30/41	236	1.8	1.4
59	UNIDENTIFIED POLYMER	98-807	FAEN	68-127	12/8/1/30/49	235	3.4	-0.1
60	UNIDENTIFIED POLYMER	100-821	LAS	34-249	20/8/1/30/41	244.249	3.1	4.1

TABLE 6A. (CONTINUED)

ITEM NO.	BUILDER TYPE AND CODE		SURFACTANT TYPE AND CODE		PROPORTIONS	SERIES REF.NO.	D E L T A W	
							BLEND FABRIC	COTTON FABRIC
61	UNIDENTIFIED POLYMER	100-821	LAS	34-249	20/8/1/50/21	249	5.3	3.0
62	UNIDENTIFIED POLYMER	100-821	FAEN	68-127	12/8/1/30/49	244,249	4.3	3.4
63	UNIDENTIFIED POLYMER	100-821	FAEN	68-127	12/8/1/50/29	249	3.8	0.5

Table 7. DETERGENCY OF MONOMERIC BUILDER - SURFACTANT FORMULATIONS
.3%, 4 washes, 200 ppm water

Item No.	Builder Type and Code	Surfactant Type and Code	Proportions	Series Ref. No.	Delta G Values: Vacuum Soil: Blend Fabric	Delta G Values: Vacuum Soil: Cotton Fabric	Delta G Values: Sebum Soil: Blend Fabric	Delta G Values: Sebum Soil: Cotton Fabric
1	Diglycollic Acid 38-279	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/30/49	45-6	2.6	.2	4.2	1.3
2	Diglycollic Acid 38-279	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/50/29	52-3	5.8	4.6	2.4	2.0
3	Diglycollic Acid 38-279	LAS 34-249	25/8/1/30/36	45-6	2.6	2.2	6.4	5.0
4	Diglycollic Acid 38-279	" "	25/8/1/50/16	52-3	4.9	1.8	3.8	2.7
5	Diglycollic Acid 40-309	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/50/29	52-3	2.0	.3	2.0	1.3
6	Diglycollic Acid 40-309	LAS 34-249	25/8/1/50/16	--[a]	6.1	2.2	5.2	2.9
7	Oxycarboxylic Acid 66-541	Fatty Alcohol Ethoxylate Nonionic 68-127	20/8D/1/30/41	122-3	1.8	1.8	1.3	2.3
8	Oxycarboxylic Acid 66-541	Alpha Olefin Sulfonate 22-155	20/8D/1/30/41	122-3	4.6	3.5	4.7	4.1
9	Oxycarboxylic Acid 66-541	LAS 34-249	20/8D/1/30/41	122-3	5.6	4.9	5.0	5.7
10	Oxycarboxylic Acid 74-596	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/60/19 low pH	137-8	1.4	.3	2.1	.8
11	Oxycarboxylic Acid 74-596	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/60/19 high pH	149-50	3.7	1.6	3.5	1.9

Table 7 (Continued)

Item No.	Builder Type and Code	Surfactant Type and Code	Proportions	Series Ref. No.	Delta G Values: Vacuum Soil: Blend Fabric	Delta G Values: Vacuum Soil: Cotton Fabric	Delta G Values: Sebum Soil: Blend Fabric	Delta G Values: Sebum Soil: Cotton Fabric
12	Monoethanolamine Carbonate 72-589	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/60/19	137-8	3.6	2.3	1.7	1.1
13	Mellitic Acid 74-606	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8D/1/30/49	147-8	4.8	.6	1.7	.9
14	Mellitic Acid 74-606	LAS 34-249	25/8D/1/50/16	147-8	2.7	2.2	1.8	2.1
15	Tetrahydrofuran Tetracarboxy Acid 76-620	Fatty Alcohol Ethoxylate Nonionic 68-127	12/8/1/30/49	149-50	1.9	.1	1.4	.6
16	Tetrahydrofuran Tetracarboxy Acid 76-620	LAS 34-249	25/8/1/50/16	153-4	1.7	1.9	1.7	3.1
17	Glucoheptonic Acid 20-151	Fatty Alcohol Ethoxylate Nonionic 68-127	20/20/1/30/29	128-9	3.6	1.0	1.4	.9
18	Citric Acid 20-152	Hydroxylated Nonionic 43-83	25/8/1/30/36	23-4	.4	.2	2.7	.7
19	Citric Acid 20-152	Fatty Alcohol Ethoxylate Nonionic 68-127	25/8/1/30/36	23-4	4.1	.6	1.7	.8
20	Citric Acid 20-152	Fatty Alcohol Ethoxylate Nonionic 68-127	20/20G/1/20/39	94-5	1.6	.8	1.3	.4
21	Citric Acid 20-152	Fatty Alcohol Ethoxylate Nonionic 68-127	20/20GD/1/20/39	94-5	2.5	.1	1.4	.5

Table 7 (Continued)

Item No.	Builder Type and Code	Surfactant Type and Code	Proportions	Series Ref. No.	Delta G Values: Vacuum Soil, Blend Fabric	Delta G Values: Vacuum Soil, Cotton Fabric	Delta G Values: Sebum Soil, Blend Fabric	Delta G Values: Sebum Soil, Cotton Fabric
22	Citric Acid 20-152	Fatty Alcohol Ethoxylate Nonionic 68-127	12/20GD/1/20/47	102-3	3.0	2.7	2.2	2.3
23	Citric Acid 20-152	Fatty Alcohol Ethoxylate Nonionic 68-127	20/20G/1/30/29	128-9	-.1	-.5	-.1	-.5
24	Citric Acid 20-152	Ether Sulfate Anionic 62-491	12/20G/1/20/47	102-3	4.0	3.9	6.8	3.1
25	Citric Acid 20-152	Ether Sulfate Anionic 62-491	12/20GD/1/20/47	102-3	5.0	4.8	7.5	3.4
26	Citric Acid 20-152	Alpha Olefin Sulfonate Anionic 22-155	20/20G/1/30/29	130-1	.1	.7	.6	.3
27	Citric Acid 20-152	Alpha Olefin Sulfonate Anionic 22-155	20/20D/1/30/29	145-6	1.7	.2	2.6	0
28	Citric Acid 20-152	Alpha Olefin Sulfonate Anionic 74-604	20/20/1/30/29	145-6	2.6	.1	2.1	0
29	Citric Acid 20-152	Ether Carboxylate Anionic 40-332	20/20D/1/30/29	155-6	1.9	-.1	.7	-.5
30	Citric Acid 20-152	Ether Carboxylate Anionic 60-486	12/20/1/20/47	102-3	3.0	3.1	6.1	3.1
31	Citric Acid 20-152	Ether Carboxylate Anionic 60-486	20/20/1/30/29	128-9	-.1	.3	-2.0	-.6
32	Citric Acid 20-152	Ether Carboxylate Anionic 78-633	20/20D/1/30/29	155-6	4.7	2.4	5.9	2.8

Table 7 (Continued)

Item No.	Builder Type and Code	Surfactant Type and Code	Proportions	Series Ref. No.	Delta G Values: Vacuum Soil: Blend Fabric	Delta G Values: Vacuum Soil: Cotton Fabric	Delta G Values: Sebum Soil: Blend Fabric	Delta G Values: Sebum Soil: Cotton Fabric
33	Citric Acid 20-152	LAS 34-249	20/20G/1/20/39	94-5	4.8	3.2	3.6	3.5
34	Citric Acid 20-152	" "	20/20GD/1/20/39	94-5	4.8	2.4	2.0	2.7
35	Citric Acid 20-152	Sulfo Zwitterionic 42-348	20/20/1/30/29	--[a]	-.1	-1.8	.2	-1.5
36	Citric Acid 20-152	" " 54-433	20/20/1/30/29	130-1	-.7	-.1	.7	-.4

a = avg. of 2.

TABLE 7A. DETERGENCY OF MONOMERIC BUILDER-SURFACTANT FORMULATIONS
.3%, SPANGLER SOIL, 3 WASHES, 200PPM WATER

ITEM NO.	BUILDER TYPE AND CODE		SURFACTANT TYPE AND CODE		PROPORTIONS	SERIES REF.NO.	DELTA W	
							BLEND FABRIC	COTTON FABRIC
37	CMOS	96-789	LAS	34-249	20/8/1/30/41	236	2.0	0.7
38	CMOS	96-789	LAS	34-249	25/8/1/30/36	237	2.9	-0.3
39	CMOS	96-789	LAS	34-249	25/8/1/50/16	237	0.7	-0.1
40	CMOS	96-789	FAEN	68-127	12/8/1/30/49	235	3.1	1.6
41	CMOS	96-789	FAEN	68-127	12/8/1/50/29	238	2.1	-0.8
42	CITRIC ACID	20-152	LAS	34-249	25/8/1/30/36	214	1.8	1.2
43	CITRIC ACID	20-152	LAS	92-752	25/8/1/30/36	224	2.5	0.1
44	CITRIC ACID	20-152	LAS	34-249	25/20/1/30/24	237	3.2	0.8
45	CITRIC ACID	20-152	FAEN	68-127	12/8/1/30/49	215	6.1	3.5
46	CITRIC ACID	20-152	FAEN	68-127	12/20/1/30/37	238	7.0	4.4
47	CARBOXYETHYL ACETONE	102-833	LAS	34-249	20/8/1/10/61	245	5.9	-1.2
48	CARBOXYETHYL ACETONE	102-833	LAS	34-249	20/8/1/50/21	245	11.4	6.8
49	CARBOXYETHYL ACETONE	102-833	FAEN	68-127	12/8/1/10/69	245	10.8	8.5
50	CARBOXYETHYL ACETONE	102-833	FAEN	68-127	12/8/1/50/29	245	9.4	5.4

Table 7B

EFFECT OF CONCENTRATION ON WHITENESS OF SOILED SWATCHES
Whiteness Units Lost as Concentration is Decreased (runs 173-196)

200 ppm Water

Durapress

Detergent	Procedure 1 Concentration			Procedure 2 Concentration			Procedure 3 Concentration			Procedure 4 Concentration			Procedure 5 Concentration		
	.3%	.2%	.1%	.3%	.2%	.1%	.3%	.2%	.1%	.3%	.2%	.1%	.3%	.2%	.1%
AATCC				0	-.6	16.5	0	1.0	16.6	0	-1.9	2.1	0	.7	5.9
AHAM				0	.7	19.9	0	.5	21.3	0	.5	7.3	0	-.4	7.2
64-1(D)				0	6.3	9.4	0	9.3	16.6	0	1.7	4.1	0	4.2	14.1
64-2(M)				0	4.5	10.8	0	5.2	14.6	0	.6	2.5	0	.7	6.1
Cotton															
AATCC	0	.4	2.8	0	-.1	7.3	0	.7	10.7	0	.1	2.3	0	-.8	3.0
AHAM	0	.7	2.5	0	0	9.6	0	.3	12.6	0	1.0	3.4	0	.5	4.5
64-1(D)	0	2.7	5.7	0	2.2	9.6	0	2.8	8.4	0	1.6	4.5	0	1.4	6.4
64-2(M)	0	-.7	5.4	0	2.1	7.8	0	1.7	7.1	0	1.4	3.8	0	.9	14.4
Tap Water															
Durapress															
AATCC				0	-1.1	6.3	0	-.8	3.9	0	-.5	-.5	0	-.3	1.2
AHAM				0	.6	8.6	0	-.1	8.4	0	-.7	1.3	0	-1.3	2.6
64-1(D)				0	4.9	12.1	0	6.8	20.1	0	1.1	3.2	0	1.8	9.5
64-2(M)				0	3.5	13.6	0	4.1	14.8	0	.5	2.3	0	-.2	4.8
Cotton															
AATCC	0	.5	1.2	0	-.4	4.5	0	-.6	3.1	0	-.1	.6	0	-1.3	-1.8
AHAM	0	-.1	-.3	0	.5	5.7	0	1.0	5.7	0	.1	.1	0	-.1	.4
64-1(D)	0	.9	5.4	0	1.4	4.8	0	1.3	7.4	0	2.1	3.1	0	.2	3.2
64-2(M)	0	.4	4.5	0	.4	3.5	0	1.0	5.6	0	-.1	2.8	0	1.8	5.2

Table 7C

EFFECT OF WATER HARDNESS ON WHITENESS OF SOILED SWATCHES

Whiteness Readings in Tap Water minus Whiteness Readings in Hard Water (200 ppm)
(Series 173-196)

Detergent	Procedure 1 Concentration .3%	 .2%	 .1%	Procedure 2 Concentration .3%	 .2%	 .1%	Procedure 3 Concentration .3%	 .2%	 .1%	Procedure 4 Concentration .3%	 .2%	 .1%	Procedure 5 Concentration .3%	 .2%	 .1%
Durapress															
AATCC				.3	.8	10.5	-.7	1.1	13.0	4.4	2.8	7.0	1.9	.5	6.6
AHAM				.4	.5	11.7	.3	.9	13.2	1.4	2.6	7.4	1.0	1.9	5.6
64-1(D)				4.8	6.2	2.1	8.7	11.2	5.2	1.6	2.2	2.5	-1.1	1.3	3.5
64-2(M)				1.5	2.5	-.3	4.0	5.1	4.6	4.2	4.3	4.4	-1.2	-.3	.1
Cotton															
AATCC	.1	0	1.7	.4	.7	3.3	1.2	2.5	8.8	2.0	1.0	3.7	1.8	2.3	6.6
AHAM	1.1	1.9	3.9	.8	.3	4.7	1.5	.8	8.4	1.0	-.1	4.3	1.7	1.3	5.8
64-1(D)	2.6	4.4	2.9	.6	1.4	5.4	5.2	6.7	6.2	2.0	1.5	3.4	.4	1.6	3.6
64-2(M)	1.3	1.4	2.2	-.7	1.0	2.6	4.4	5.1	5.9	.8	2.1	1.8	1.0	.1	.2

TABLE 8. REPRESENTATIVE DRUM-DRIER FORMULATIONS OF SATISFACTORY CHARACTER[a]

1. 30 parts NTA; 20 parts alpha olefin sulfonate surfactant 22-155; 1 part NaCMC; 8 parts silicate D; 41 parts sodium sulfate (Formulation Ref. No. 64-511).
2. 30 parts SAND; 20 parts ether carboxylate surfactant 60-486; 1 part NaCMC; 8 parts silicate D; 41 parts sodium sulfate (Formulation Ref. No. 64-515).
3. 30 parts SAND; 20 parts ether sulfate surfactant 62-491; 1 part NaCMC; 8 parts silicate D; 41 parts sodium sulfate (Formulation Ref. No. 64-514).
4. 30 parts SAND; 15 parts fatty alcohol ethoxylate nonionic surfactant 68-127; 1 part NaCMC; 8 parts silicate D; 46 parts Na_2SO_4 (Formulation Ref. No. 64-516).
5. 30 parts sodium citrate; 20 parts silicate G; 20 parts sulfo zwitterionic surfactant 54-433; 1 part NaCMC; 29 parts sodium sulfate (Formulation Ref. No. 64-2).
6. 30 parts sodium citrate; 20 parts silicate G; 20 parts sulfo zwitterionic surfactant 42-348; 1 part NaCMC; 29 parts sodium sulfate (Formulation Ref. No. 67-1).
7. 30 parts sodium citrate; 20 parts silicate G; 20 parts ether carboxylate anionic surfactant 60-486; 1 part NaCMC; 29 parts sodium sulfate (Formulation Ref. No. 64-1).

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[a] Fluorescent whitening agents and minor adjuvants can be added as desired without essentially changing the physical character of the product. Tendency to cake in storage, as a function of pressure and humidity, not investigated.

TABLE 8a. REPRESENTATIVE LIQUID FORMULATIONS OF SATISFACTORY CHARACTER[a]

1. 10.6 parts fatty alcohol ethoxylate nonionic surfactant 68-127; 16 parts sodium citrate; 11 parts silicate D; 10 parts di-sodium octenyl succinate; water q.s. 100 (Formulation Ref. No. 73).
2. 14 parts ether carboxylate anionic surfactant 40-332; 5.7 parts silicate D; 22 parts SHIM; 10 parts sodium xylene sulfonate (Formulation Ref. No. 71).
3. 10 parts fatty alcohol ethoxylate nonionic surfactant 68-127; 6.7 parts silicate N; 25 parts SHIM; 4.5 parts di-sodium octenyl succinate; water q.s. 100 (Formulation Ref. No. 59-1).
4. 12 parts alpha olefin sulfonate anionic surfactant 22-155; 4.8 parts silicate D; 18 parts SHIM; 7.7 parts sodium xylene sulfonate; water q.s. 100 (Formulation Ref. No. 65-1).
5. 12 parts alpha olefin sulfonate anionic surfactant 22-155; 4.8 parts silicate D; 18 parts SHIM; 5.6 parts sodium xylene sulfonate; 8 parts isopropanol; water q.s. 100 (Formulation Ref. No. 60-1).

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[a] NaCMC does not dissolve readily in these formulations, but can be suspended with or without other anti-redeposition agents and auxiliaries. About 1 part NaCMC per 15-20 parts surfactant is a suitable proportion.

Table 9. STIMULATORY EFFECT ON GROWTH OF ALGAE

(Positive is stimulating - negative is inhibiting.)

Item #	Code #	Class of Compound	SPECIES Anabaena	Microcystis	Selenastrum	Navicula
1	20-146	Low titer soap	Slightly positive at 10 ppm. No effect at 0.1 and 1 ppm.	No effect at 1 and 10 ppm.	---	No effect at 0.1, 1, and 10 ppm.
2	22-155	Alpha Olefin Sulfonate	---	No effect at 1 and 10 ppm.	No effect at 1 ppm	No effect at 0.1 and 1 ppm. Slightly positive at 10 ppm.
3		Sodium Metasilicate	No effect at 7 ppm. Negative at 35 and 70 ppm.	No effect at 50 ppm.	No effect at 1 ppm.	Excess over amount in medium has no effect.
4	43-83	Hydroxylated Nonionic	No effect at 5 ppm.	No effect at 1 ppm.	No effect at 1 ppm.	No effect at 1 ppm.
5	68-127	Fatty Alcohol Ethoxylate	No effect at 5 ppm.	Slightly negative at 5 ppm.	---	---
6	68-134	Fatty Alcohol Ethoxylate	Slightly negative at 1 ppm.	---	---	No effect at 1 ppm.

Table 9 (Continued)

			SPECIES			
Item #	Code #	Class of Compound	Anabaena	Microcystis	Selenastrum	Navicula
7	20-138	Fatty Alcohol Ethoxylate	No weight effect, but cells altered at 0.5 and 5 ppm.	No effect at 0.5 and 5 ppm.	No effect at 0.5 and 5 ppm.	---
8	43-64	Commercial High Carbonate Detergent	No effect at 5 ppm.	Negative at 5 ppm.	Slightly negative at 5 ppm.	No effect at 5 ppm.
9	54-433	Zwitter-ionic Sulfonate	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.
10	42-348	Zwitter-ionic Sulfonate	Slightly negative at 1 ppm. No effect at 0.1 ppm.	Slightly negative at 1 ppm. No effect at 0.1 ppm.	Slightly negative at 1 ppm. No effect at 0.1 ppm.	No effect at 0.1 and 1 ppm.
11	56-445	SHIM (HEIDA)	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.
12	40-312	SAND	No effect at 1 and 5 ppm.	No effect at 5 ppm. Slightly negative at 1 ppm.	No effect at 5 ppm. Slightly negative at 1 ppm.	No effect at 1 and 5 ppm.
13	38-279	Diglycollic Acid	No effect at 1 and 5 ppm.	No effect at 1 ppm. Slightly positive at 5 ppm.	No effect at 1 and 5 ppm.	No effect at 1 and 5 ppm.

Table 9 (Continued)

			SPECIES			
Item #	Code #	Class of Compound	Anabaena	Microcystis	Selenastrum	Navicula
14	60-486	Ether carboxylate anionic surfactant	No effect at 1.0 ppm. Slightly negative at 0.1 ppm.	No effect at 1.0 and 5.0 ppm.	No effect at 1.0 and 5.0 ppm.	No effect at 1.0 and 10.0 ppm. Slightly negative at 0.1 ppm.
15	90-730	Anionic sulfonate surfactant	No effect at 1.0 and 10.0 ppm.	No effect at 1.0 ppm. Slightly positive at 10.0 ppm.	No effect at 1.0 ppm. Slightly positive at 10.0 ppm.	No effect at 1.0 ppm. Very slightly negative at 10 ppm.
16	86-700	Standard phosphate built detergent	No effect at 10.0 and 20.0 ppm.	Positive (400%) at 10.0 ppm. Positive (250%) at 20.0 ppm.	Positive (200%) at 10.0 and 20.0 ppm.	No effect at 10.0 ppm. Very slightly positive at 20.0 ppm.
17	80-647	Monomeric builder CMOS	No effect at 1.0 ppm. Slightly negative at 10.0 ppm.	No effect at 1.0 and 10.0 ppm.	No effect at 1.0 and 10.0 ppm.	No effect at 1.0 and 10.0 ppm.
18	20-147	High titer soap	---	No effect at 1.0 and 10.0 ppm.	---	No effect at 1.0 ppm. Slightly negative at 10.0 ppm
19	34-249	LAS anionic surfactant	No effect at 1.0 and 10.0 ppm.	No effect at 1.0 and 10.0 ppm.	No effect at 1.0 ppm. Very slightly negative at 10.0 ppm.	No effect at 1.0 ppm. Positive (163%) at 10.0 ppm.

Table 10

ACUTE AQUATIC TOXICITY OF DETERGENTS AND THEIR INGREDIENTS

Item No.	Code	Description	96 hr. TLm Fish ppm.	96 hr. TLm Snail ppm.	ppm. to cause 50% redn. in growth, 7 days Diatom
1	20-151	Glucoheptonic acid	>2000	>2000	>1800
2	20-152	Sodium citrate	1710	1415	1200
3	20-138	Fatty alcohol ethoxylate nonionic surfactant	2.87	23.1	4.5
4	43-67	Fatty alcohol ethoxylate nonionic surfactant	3.45	6.01	185
5	68-127	Fatty alcohol ethoxylate nonionic surfactant	3.87	6.1	313
6	51-101	Fatty alcohol ethoxylate nonionic surfactant	3.95	4.03	900
7	51-100	Fatty alcohol ethoxylate nonionic surfactant	2.73	4.3	270
8	68-134	Fatty alcohol ethoxylate nonionic surfactant	2.89	3.33	625
9	51-93	Fatty alcohol ethoxylate nonionic surfactant	3.7	9.5	123
10	43-64	Commercial detergent-high carbonate type	26.7	25.8	155
11	26-189	Hydroxylated nonionic surfactant	14.8	> 490	890
12	26-191	Hydroxylated nonionic surfactant	196	89.5	125
13	43-83	Hydroxylated nonionic surfactant	37	165	100
14	38-279	Diglycollic acid builder	> 490	> 490	750
15	20-141	Polymeric builder	680	420	62
16	42-353	Sulfo zwitterionic surfactant	.76	1.0	3.8
17	54-433	Sulfo zwitterionic surfactant	7.7	6.6	35

Table 10 (Continued)

18	46-356	Carboxy zwitterionic surfactant	10.5	13.3	16.4
19	40-332	Ether carboxy anionic surfactant	3.15	4.7	64.5
20	48-373	Amine oxide surfactant	3.7	3.8	6.0
21	22-155	Alpha olefin sulfonate anionic surfactant	4.25	6.8	24.2
22	62-491	Ether sulfonate anionic surfactant	.57	.84	25
23	18-136	NTA builder	500	500	500
24	64-511	Formulation of 22-155 and NTA	10.0	15.6	54.9
25	40-312	SAND builder	490	490	870
26	56-445	SHIM builder	> 100	> 100	> 100
27	64-1	Citrate formulation with 60-486 surfactant	23.7	24.0	> 100
28	64-2	Citrate formulation with 54-433 surfactant	20.2	98.1	21.6
29	67-1	Citrate formulation with 42-348 surfactant	44.0	56.0	22.1
30	80-647	CMOS monomeric builder	> 560	> 560	229% growth at 100 ppm (a)
31	90-730	D-116 anionic surfactant	20.5	32.3	17.3
32	104-860	POCNa polymeric builder	> 560	> 560	> 560
33	100-823	Calnox 214 DN polyacrylic builder	> 560	> 560	300% growth at 100 ppm (a)
34	106-866	Maleic telomer builder	> 560	> 560	890% growth at 100 ppm (a)

(a) These figures indicate stimulation of growth.

Table 11

ESTIMATION OF BIODEGRADABILITY OF MATERIALS USED IN DETERGENT FORMULATIONS

I. Materials considered biodegradable

Code No.	Type
43-83	Hydroxylated nonionic surfactant
40-332	Ether carboxylate anionic surfactant
42-348	Sulfo zwitterionic surfactant
38-279	Diglycollic acid builder
66-541	Monomeric builder
74-606	Monomeric builder, Mellitic acid
56-445	SHIM builder
80-647	Monomeric builder, CMOS
60-486	Ether carboxylate surfactant
20-145	Sugar ester surfactant
90-730	Anionic sulfonate surfactant
104-860	Polymeric builder, hydroxylated acrylic

II. Materials considered non-biodegradable

Code No.	Type
76-620	Monomeric builder
43-65	Polymeric builder
66-530	Polymeric carbohydrate type builder
74-602	Polymeric carbohydrate type builder
58-466	Polymeric builder
86-709	Polymeric builder, maleic copolymer
40-310	Polymeric builder, maleic copolymer
92-745	Polymeric builder, acrylic
43-74	Polymeric builder, acrylic
98-806	Polymeric builder
98-807	Polymeric builder
100-824	Polymeric builder, acrylic
100-822	Polymeric builder, carbohydrate
106-871	Polymeric builder, maleic
102-833	Monomeric builder

Table 11 (Continued)

III. Materials of questionable (slow or incomplete) biodegradability

Code No.	Type
100-821	Polymeric builder
100-823	Polymeric builder, acrylic
102-834	Polymeric builder, carbohydrate
106-866	Polymeric builder, maleic telomer

Table 12

HAZARD TEST RESULTS. DETERGENT FORMULATIONS

Ident. No.	LD50 ORAL mg/kg	LD50 DERMAL mg/kg	Rabbit skin irrit.score	Rabbit eye irrit.(b)	Esophageal irrit.	Human patch test(c)
64-2	> 5	> 2	2.54	irrit. (39,25,21)	equal to sucrose control	negative
65-1	< 5	> 2	> 5.5	irrit. (27,27,22)	----	----
65-2	> 10	0.99(a)	4.0	irrit. (32,26,19)	----	----
64-1	> 10	> 2	2.9	irrit. (35,27,22)	equal to sucrose control	negative
67-1	4.13 (m) 3.55 (f)	> 1, < 2(a)	----	irrit. (50,47,38)	equal to sucrose control	----
56-445	2.61 (m) 3.83 (f)	3.21(a)	----	----	----	----
43-64	----	----	----	----	very slight positive	negative
LP-23	> 5	> 2	0.38	----	----	----
LP-24	> 5	> 2	----	----	----	----
LP-25	> 5	> 2	----	----	----	----

(a) Wide variation; severe renal damage.

(b) Figures are eye scores at 24, 48 and 72 hours.

(c) Five week repeated insult patch test on 53 panelists.

Table 12a

IDENTIFICATION OF FORMULATIONS IN Table 12

Ident No.	Composition
64-2	20/20/1/30/29. Surfactant 54-433, Builder citrate, Solid.
65-1	12/4.8/0/18/7.7/qs H_2O. Surfactant 22-155, Builder SHIM, Hydrotrope Na xylene sulfonate, Liquid.
65-2	10/6.7/0/25/4.5/qs H_2O. Surfactant 68-127, Builder SHIM, Hydrotrope Na octenyl succinate, Liquid.
64-1	20/20/1/30/29. Surfactant 60-486, Builder citrate, Solid.
67-1	20/20/1/30/29. Surfactant 42-348, Builder citrate, Solid.
56-445	SHIM (HEIDA) builder, 25% aqueous solution.
43-64	Commercial phosphate-free, high carbonate detergent.
LP-23	Sodium xylene sulfonate, 20% aqueous solution.
LP-24	Sodium octenyl succinate, 5% aqueous solution.
LP-25	Sodium nitrilotriacetate (NTA), 25% aqueous solution.

Table 13

EFFECT OF MULTIPLE WASHINGS ON BUILD UP OF IMPURITIES IN FABRIC

		Alcohol Extractable* Content of Fabric, %				Ash Content* of Fabric, %			
		After 20 Washings		After 50 Washings		After 20 Washings		After 50 Washings	
Ident. Number	Detergent Type	Blend Fabric	Cotton	Blend Fabric	Cotton	Blend Fabric	Cotton	Blend Fabric	Cotton
86-700	AATCCWOB	.30	.77	.64	.36	.29	.09	.36	.08
88-722	Commercial high carbonate	--	--	.54	.40	--	--	7.5	10.6
88-726	Commercial high silicate	--	--	.61	.50	--	--	.80	.41
86-706	Soap & lime soap disperser	.74	1.49	2.39	2.33	.37	.13	.56	.39
86-707	Soap & lime soap disperser	1.43	2.41	2.20	2.12	.39	.24	--	--
86-708	Soap & lime soap disperser	1.14	1.47	--	--	.39	.19	.54	--
20-147	Soap & silicate 85/15/0/0/0	2.09	3.31	3.50	5.71	.50	.60	.77	1.19
---	None-Hard Water Alone	.58	.58	.78	.61	.28	.03	.31	.08

* Original unwashed blend fabric averaged .81% alcohol extractable and .33% ash.
Original unwashed cotton fabric averaged .47% alcohol extractable and .05% ash.

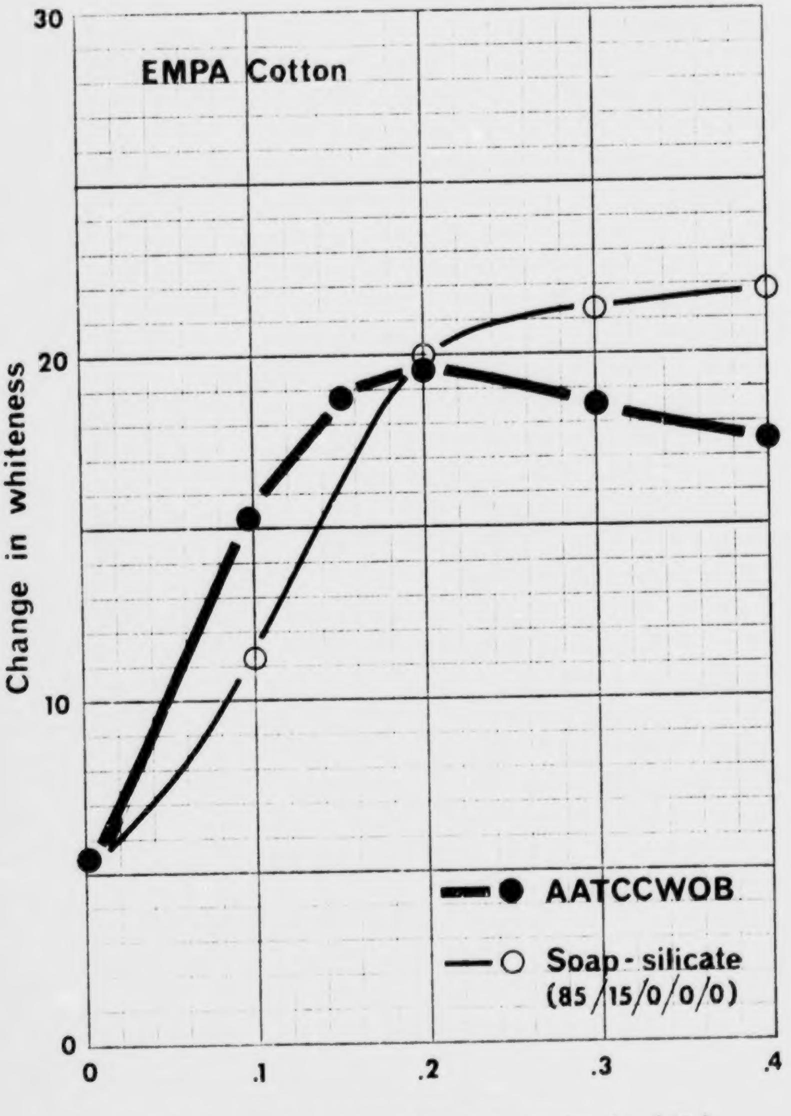

Figure 1. Detergency v. concentration. Item 20-147 high titer soap. Series ref. 210. Empa soil. 200 ppm water.

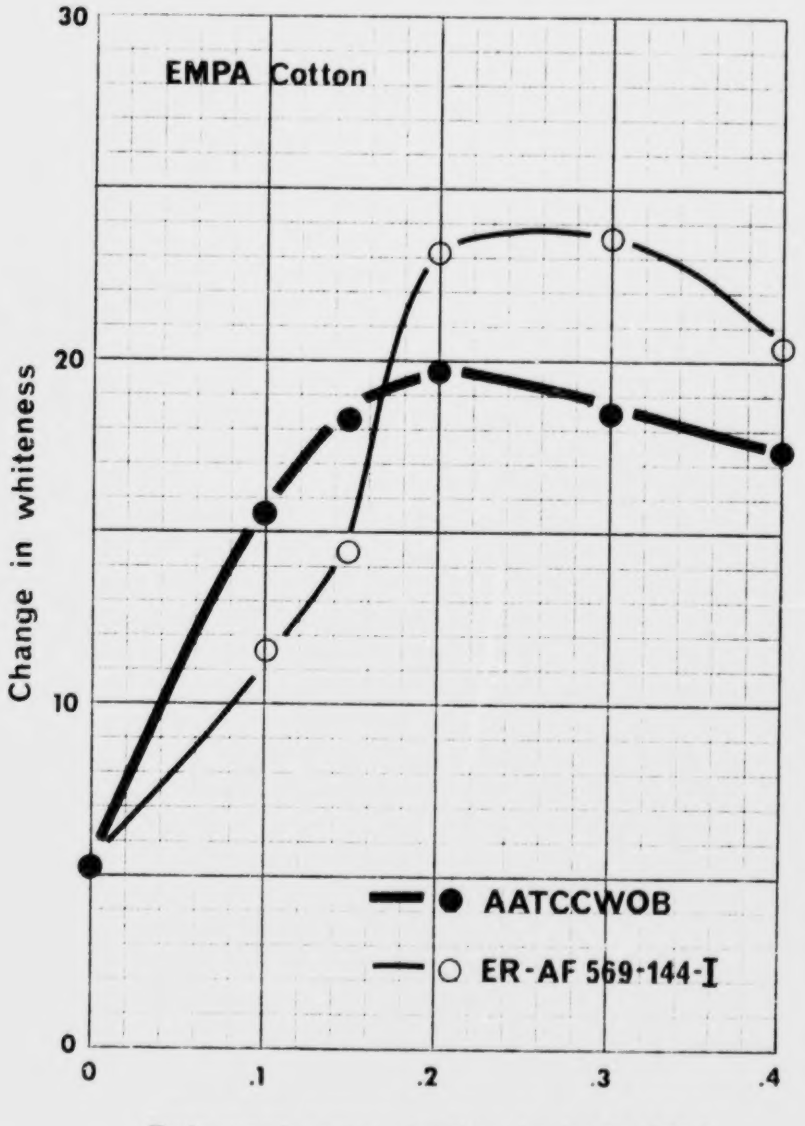

Figure 2. Detergency v. concentration. Item 86-706. Soap-lime soap disperser. Series ref. 210. Empa soil. 200 ppm water.

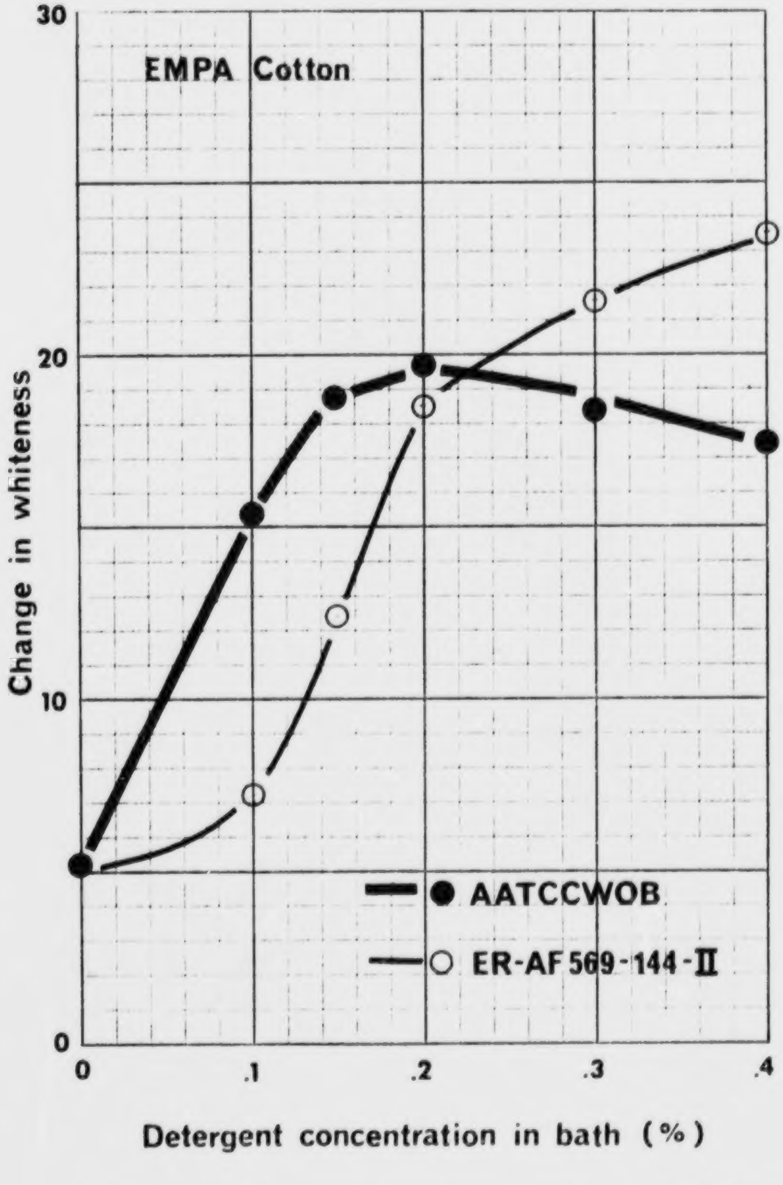

Figure 3. Detergency v. concentration. Item 86-707. Soap-lime soap disperser. Series ref. 210. Empa soil. 200 ppm water.

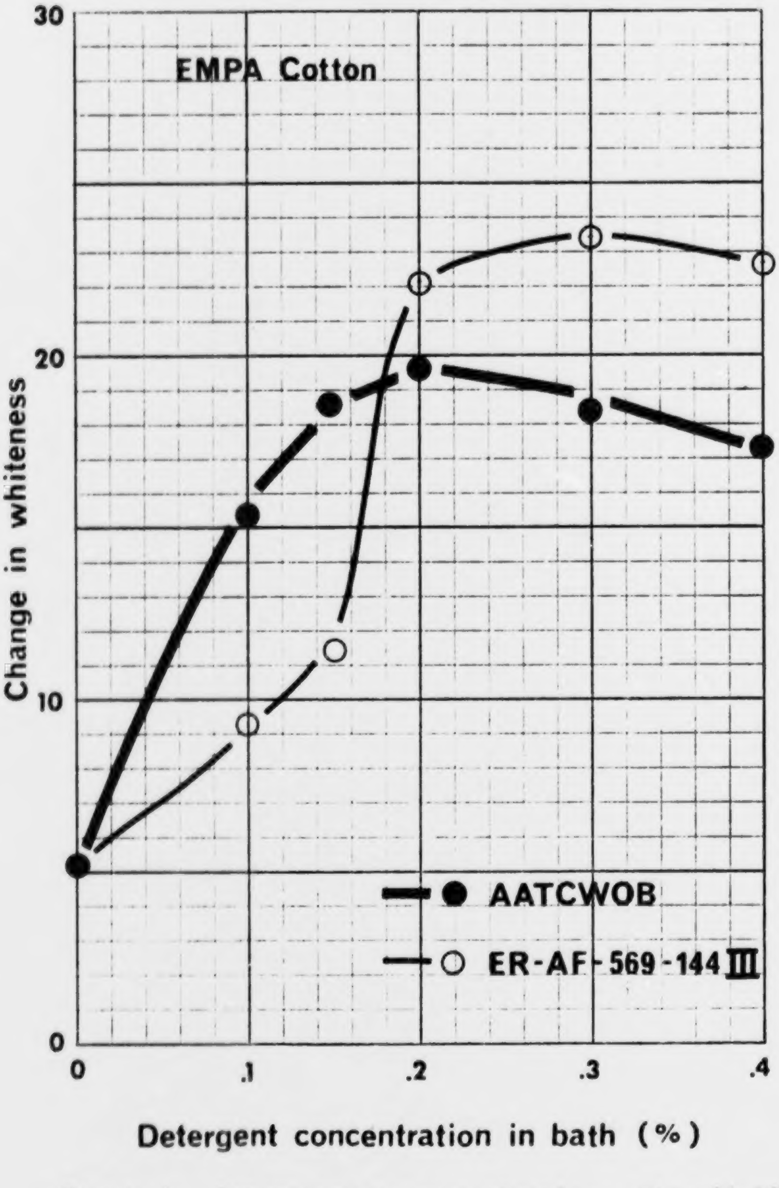

Figure 4. Detergency v. concentration. Item 86-708. Soap-lime soap disperser. Series ref. 210. Empa soil. 200 ppm water.

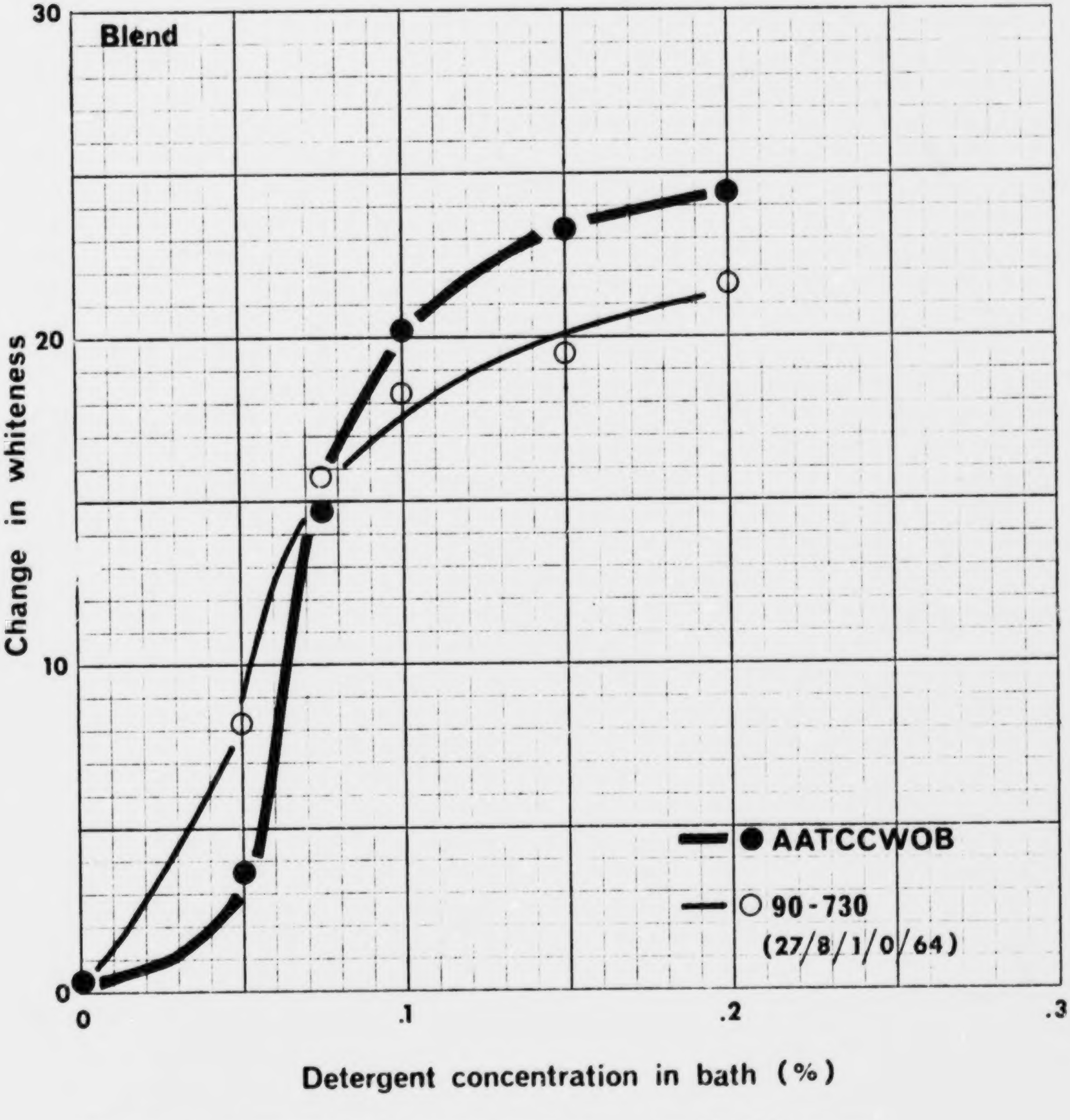

Figure 5. Detergency v. concentration. Item 90-730 anionic sulfonate. Series ref. 243. Colgate soil. Tap water. Blend fabric.

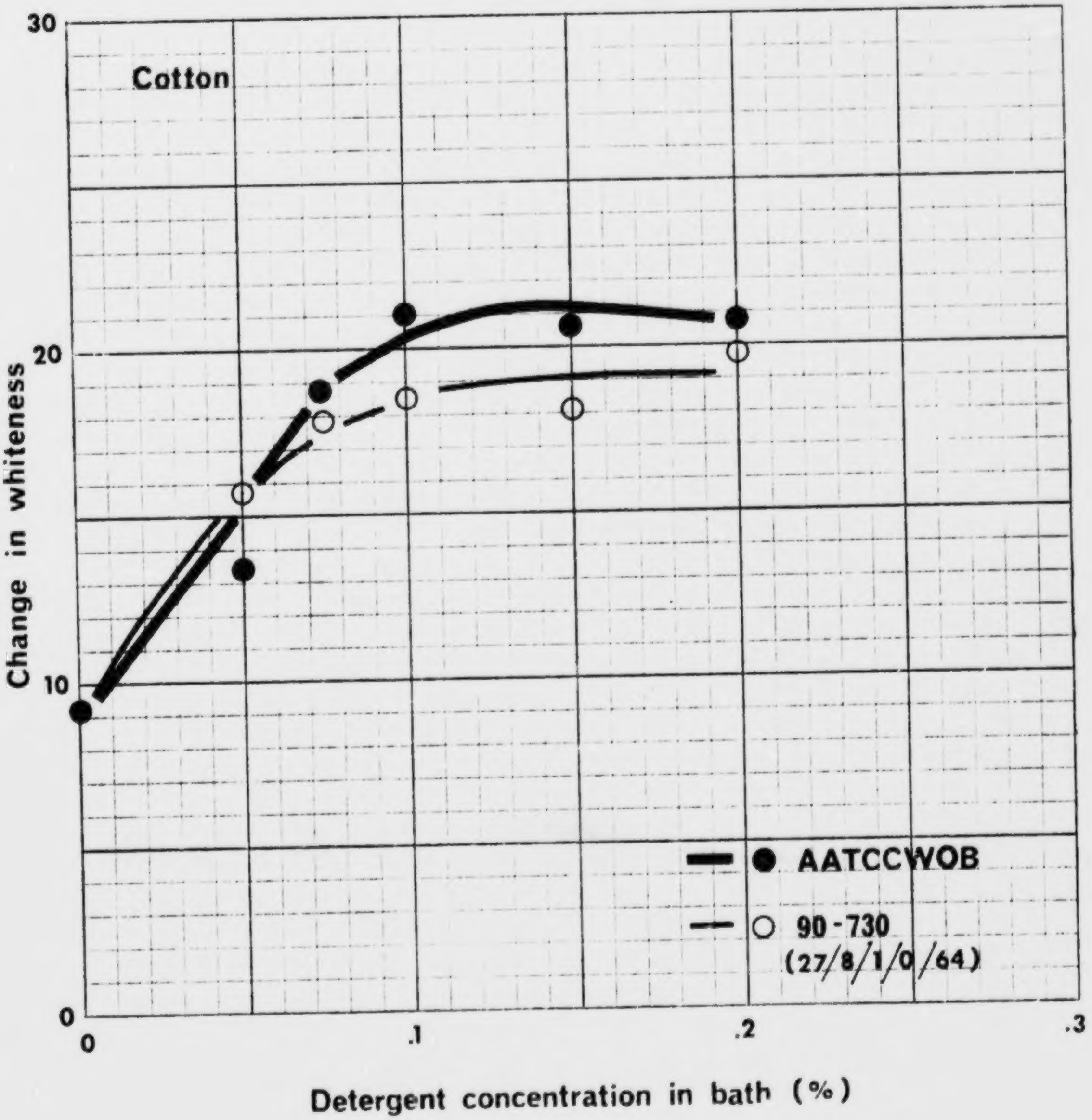

Figure 6. Detergency v. concentration. Item 90-730 anionic sulfonate. Series ref. 243. Colgate soil. Tap water. Cotton.

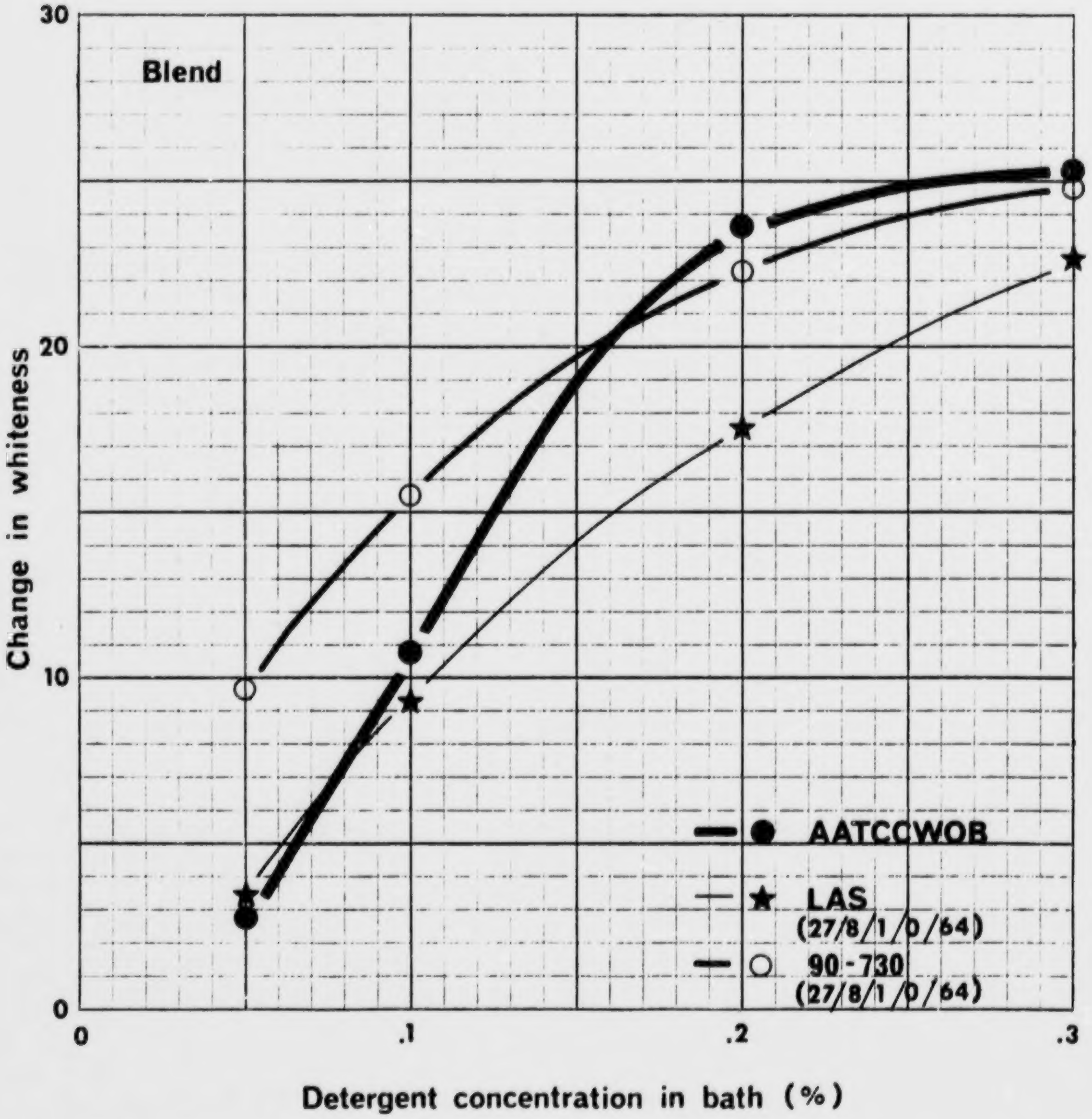

Figure 7. Detergency v. concentration. LAS and Item 90-730 anionic sulfonate. Series ref. 239C. Colgate soil. 200 ppm water. Blend fabric.

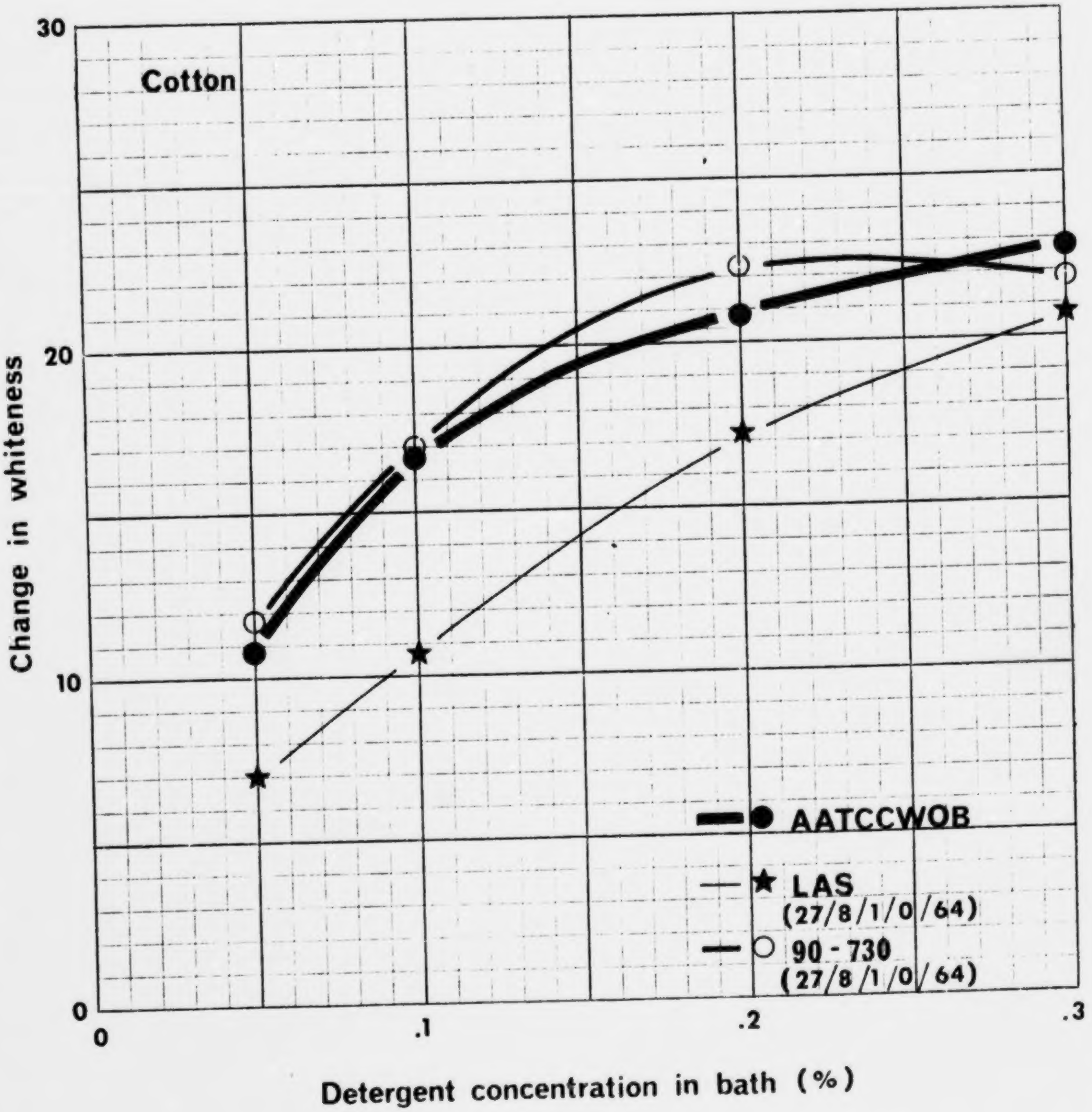

Figure 8. Detergency v. concentration. LAS and Item 90-730 anionic sulfonate. Series ref. 239C. Colgate soil. 200 ppm water. Cotton.

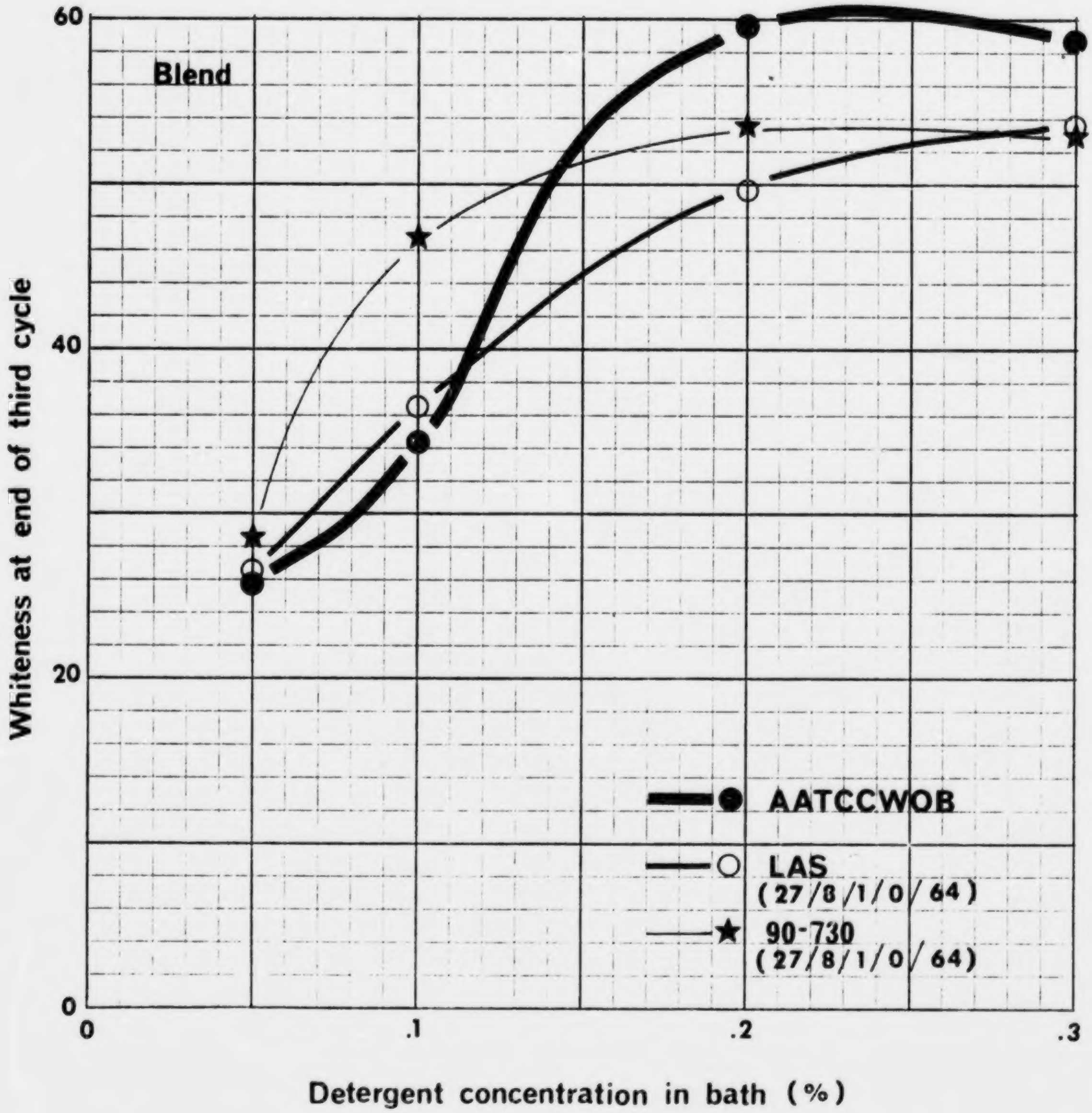

Figure 9. Detergency v. concentration. LAS and Item 90-730 anionic sulfonate. Series ref. 239. Spangler soil multicycle. 200 ppm water. Blend fabric.

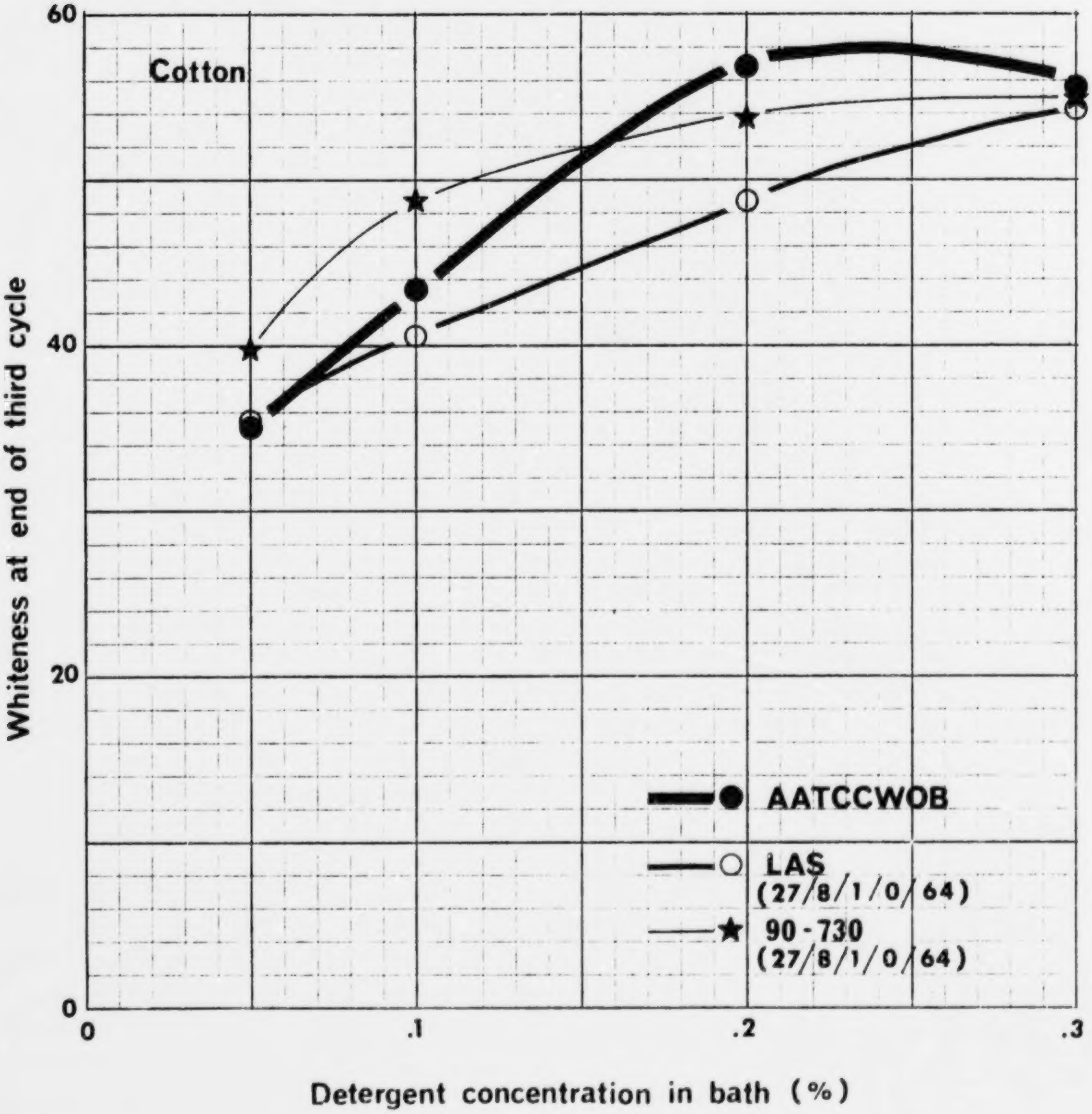

Figure 10. Detergency v. concentration. LAS and Item 90-730 anionic sulfonate. Series ref. 239. Spangler soil multicycle. 200 ppm water. Cotton.

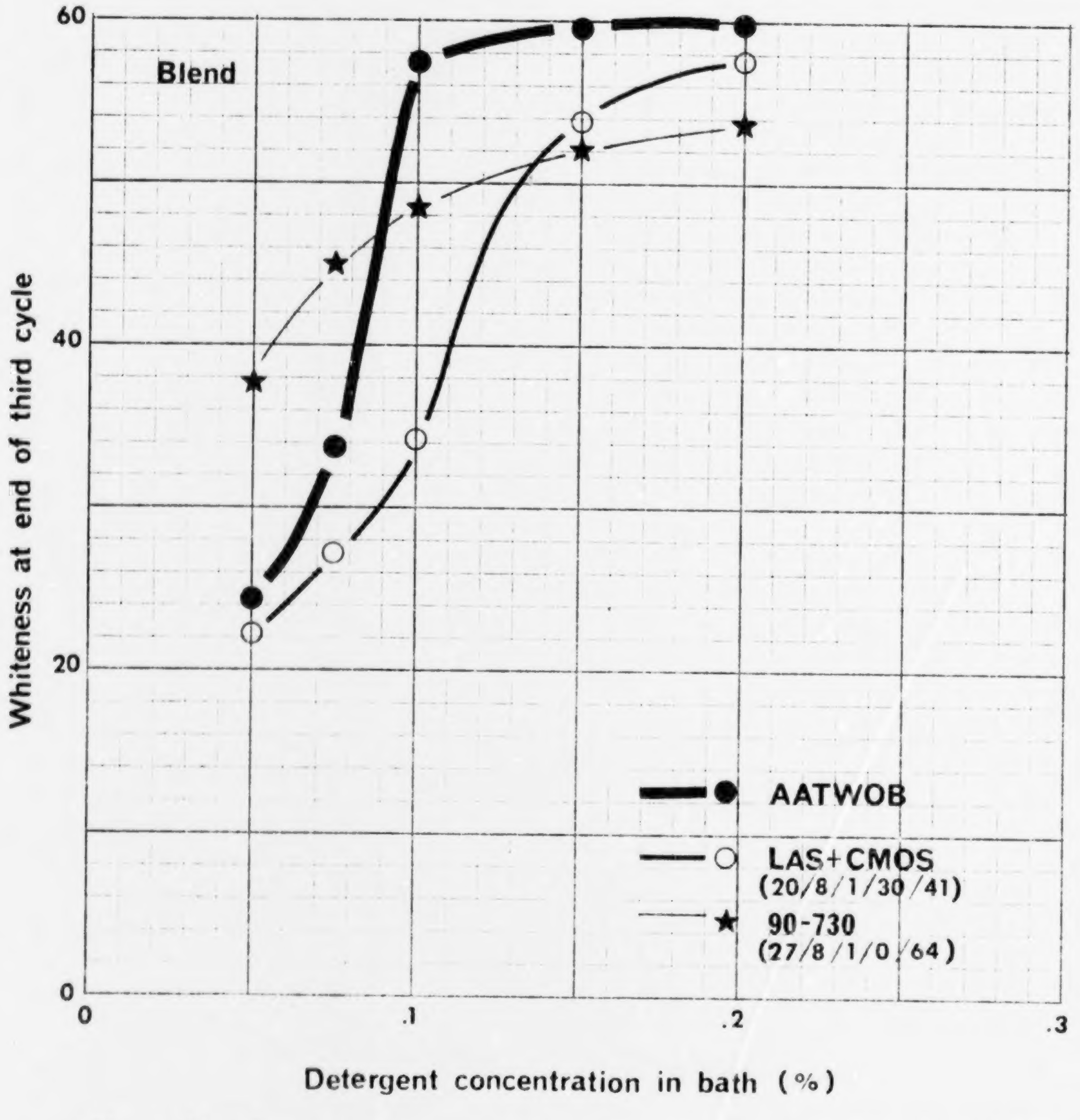

Figure 11. Detergency v. concentration. LAS and LAS-CMOS (item 80-647) and Item 90-730 anionic sulfonate. Series ref. 243. Spangler soil multicycle. Tap water. Blend fabric.

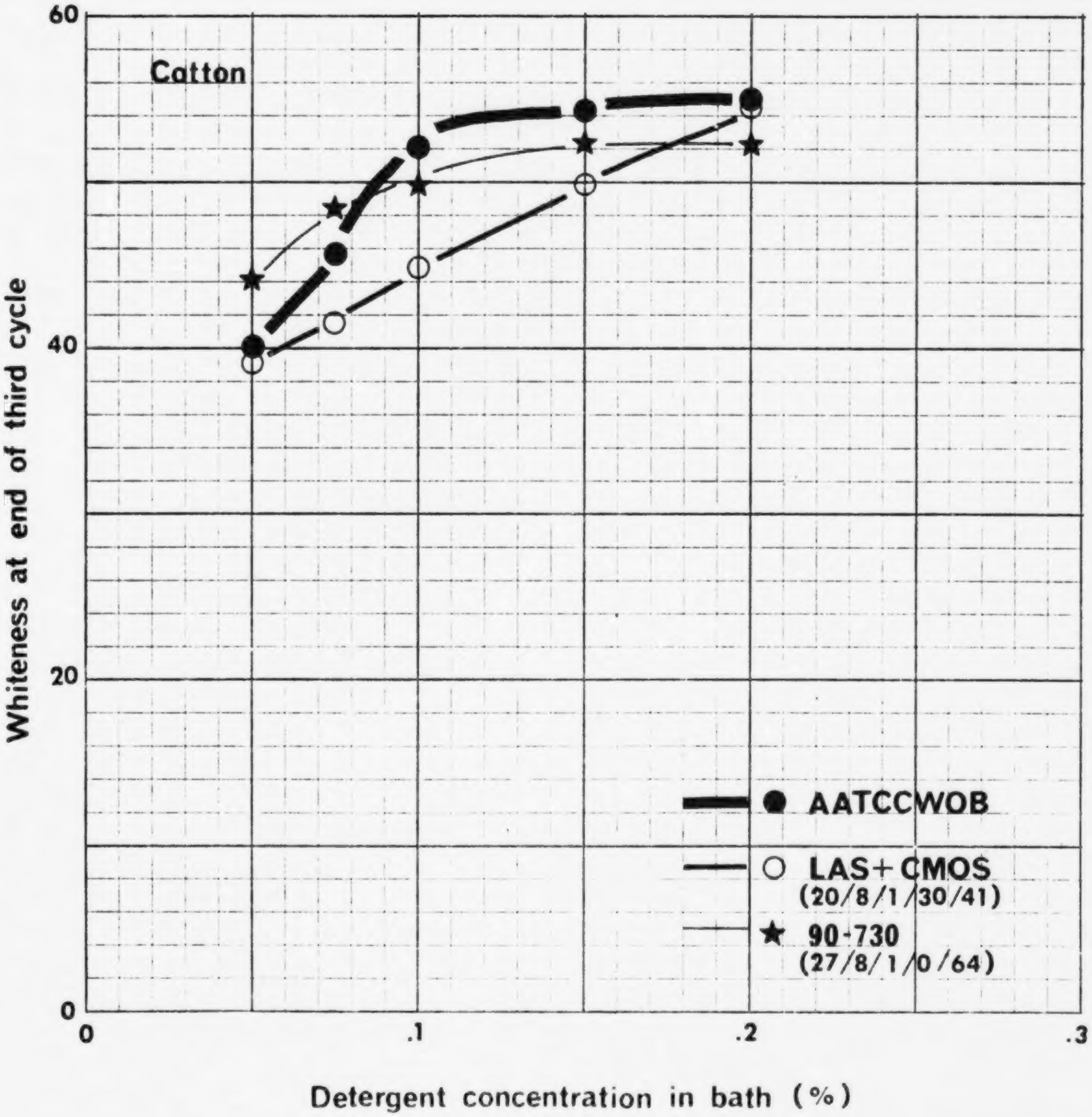

Figure 12. Detergency v. concentration. LAS and LAS-CMOS (item 80-647) and Item 90-730 anionic sulfonate. Series ref. 243. Spangler soil multicycle. Tap water. Cotton.

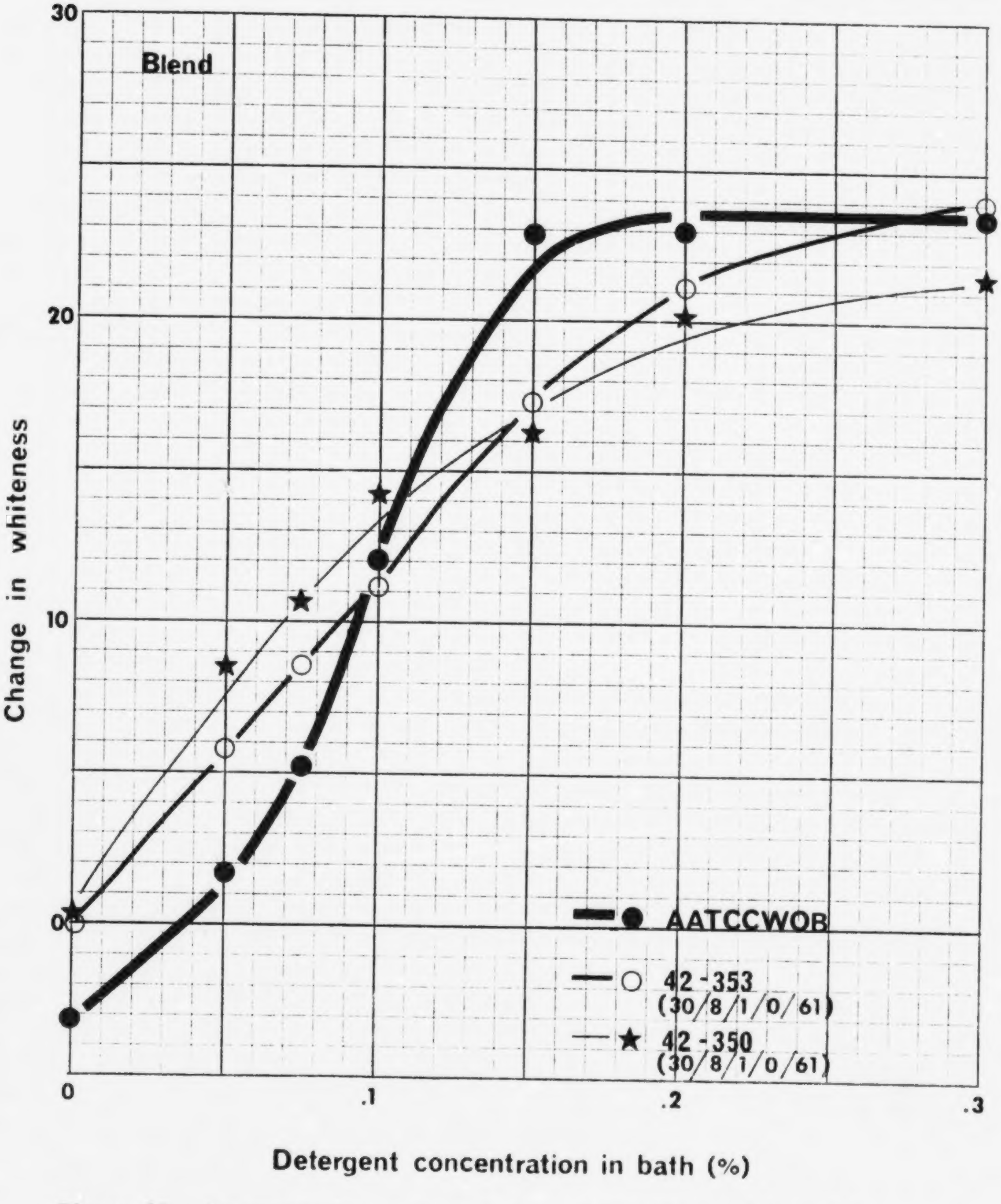

Figure 13. Detergency v. concentration. Items 42-350 and 42-353 zwitterionic. Series ref. 247 and 252 (for AATCCWOB). Colgate soil. 200 ppm water. Blend fabric.

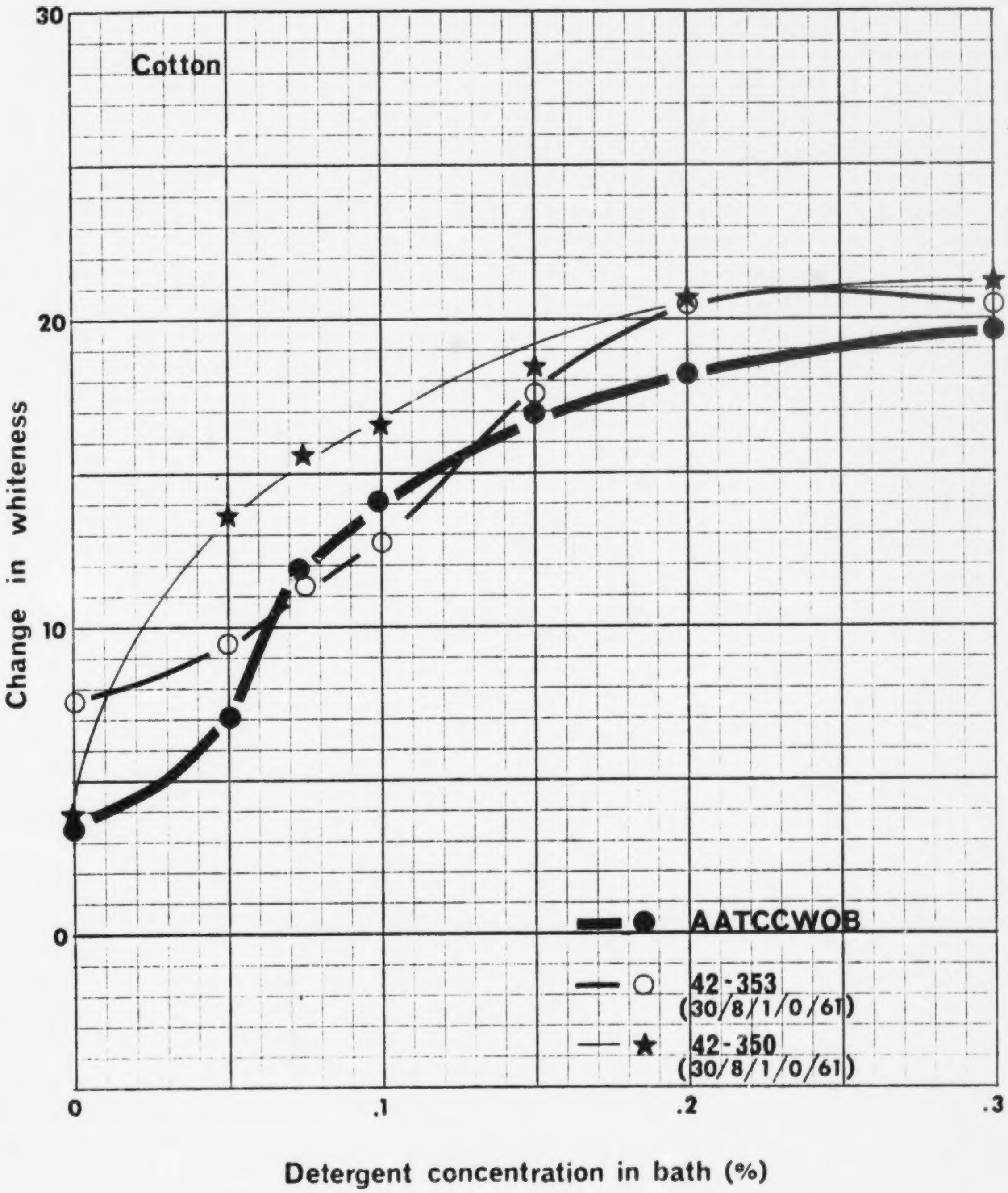

Figure 14. Detergency v. concentration. Items 42-350 and 42-353 zwitterionic. Series ref. 247 and 252 (for AATCCWOB). Colgate soil. 200 ppm water. Cotton.

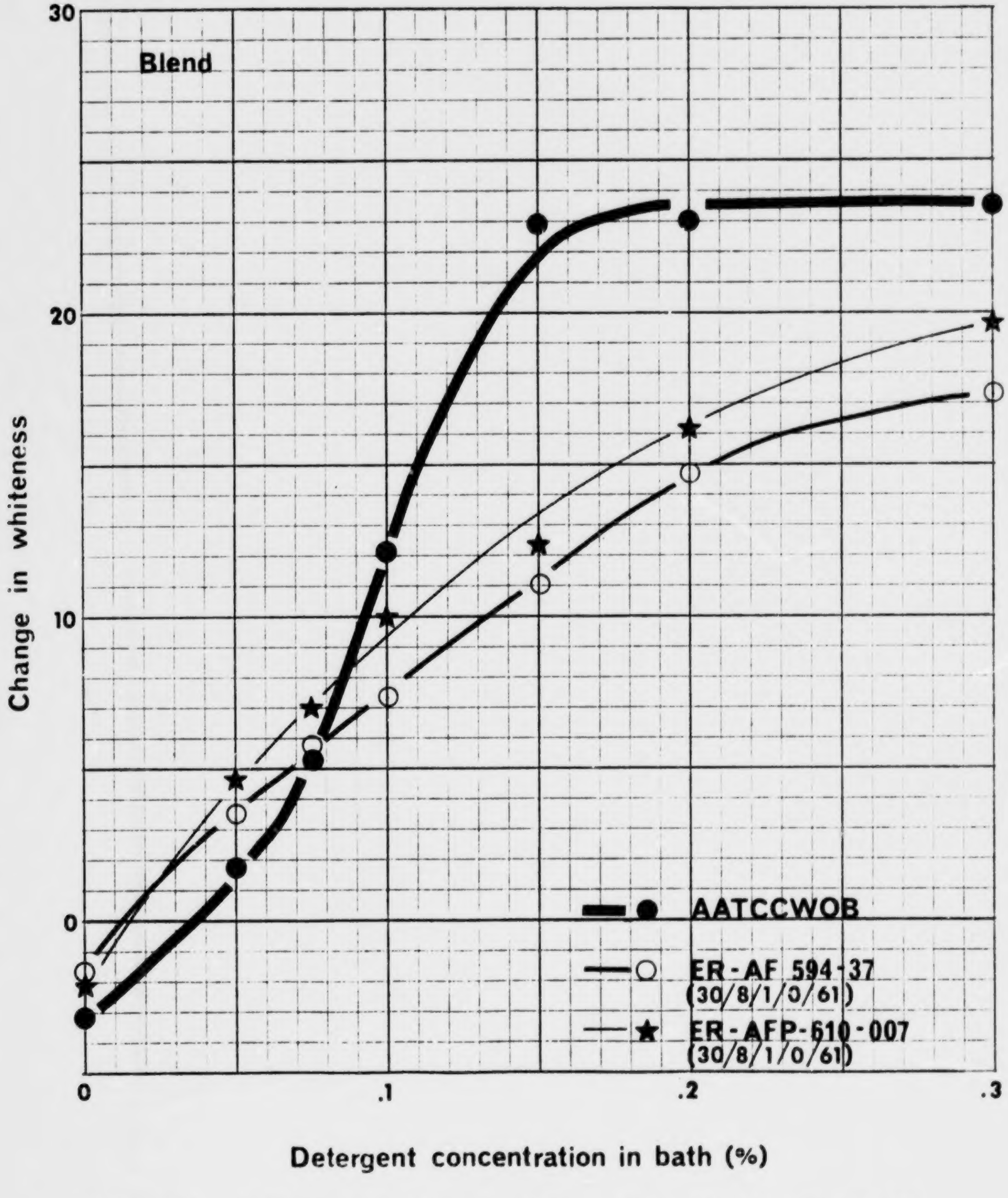

Figure 15. Detergency v. concentration. Items 104-856 and 108-880 anionics. Series refs. 252 (AATCCWOB) 250 and 256. Colgate soil. 200 ppm water. Blend fabric.

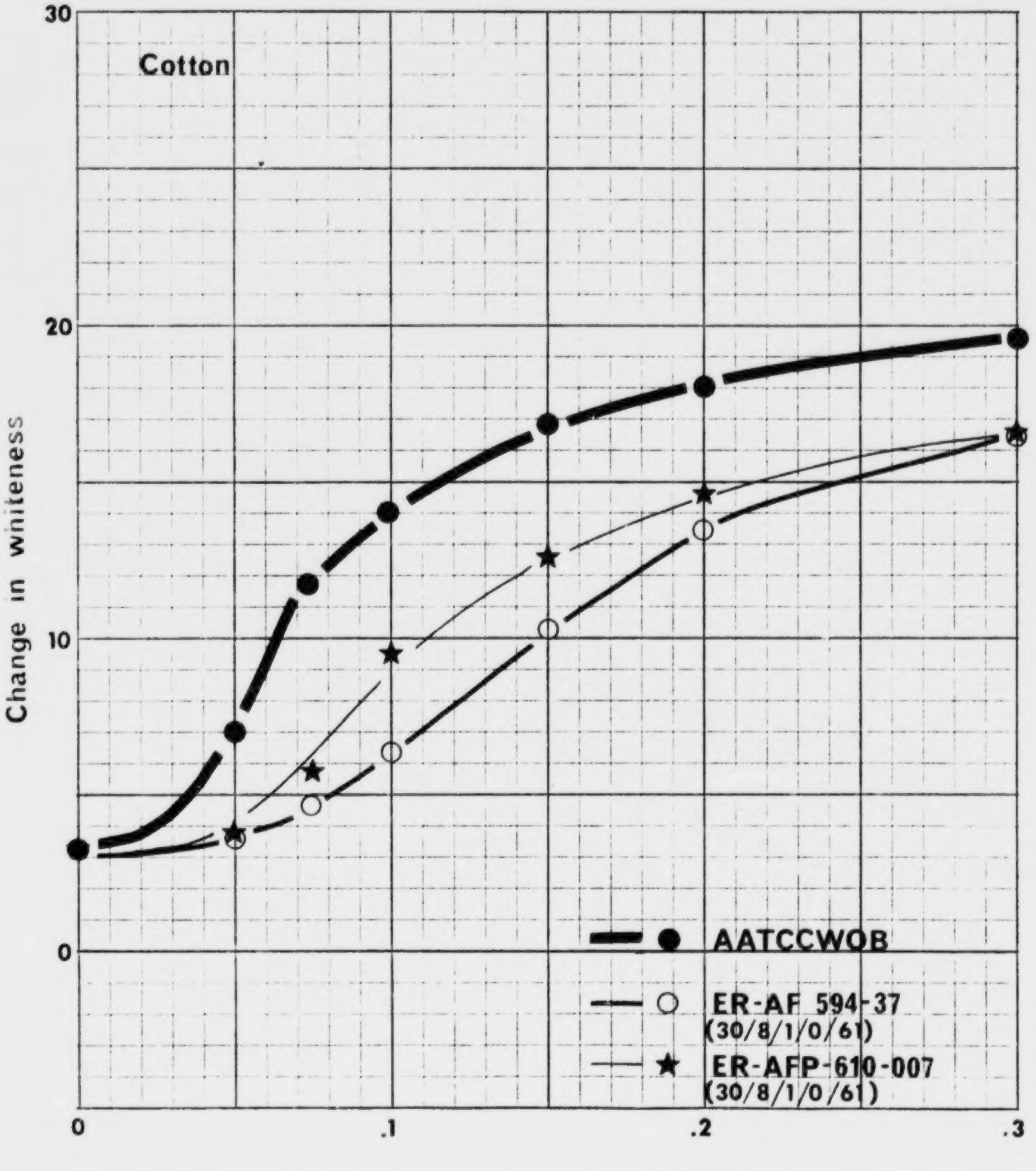

Figure 16. Detergency v. concentration. Items 104-856 and 108-880 anionics. Series refs. 252 (AATCCWOB) 250 and 256. Colgate soil. 200 ppm water. Cotton.

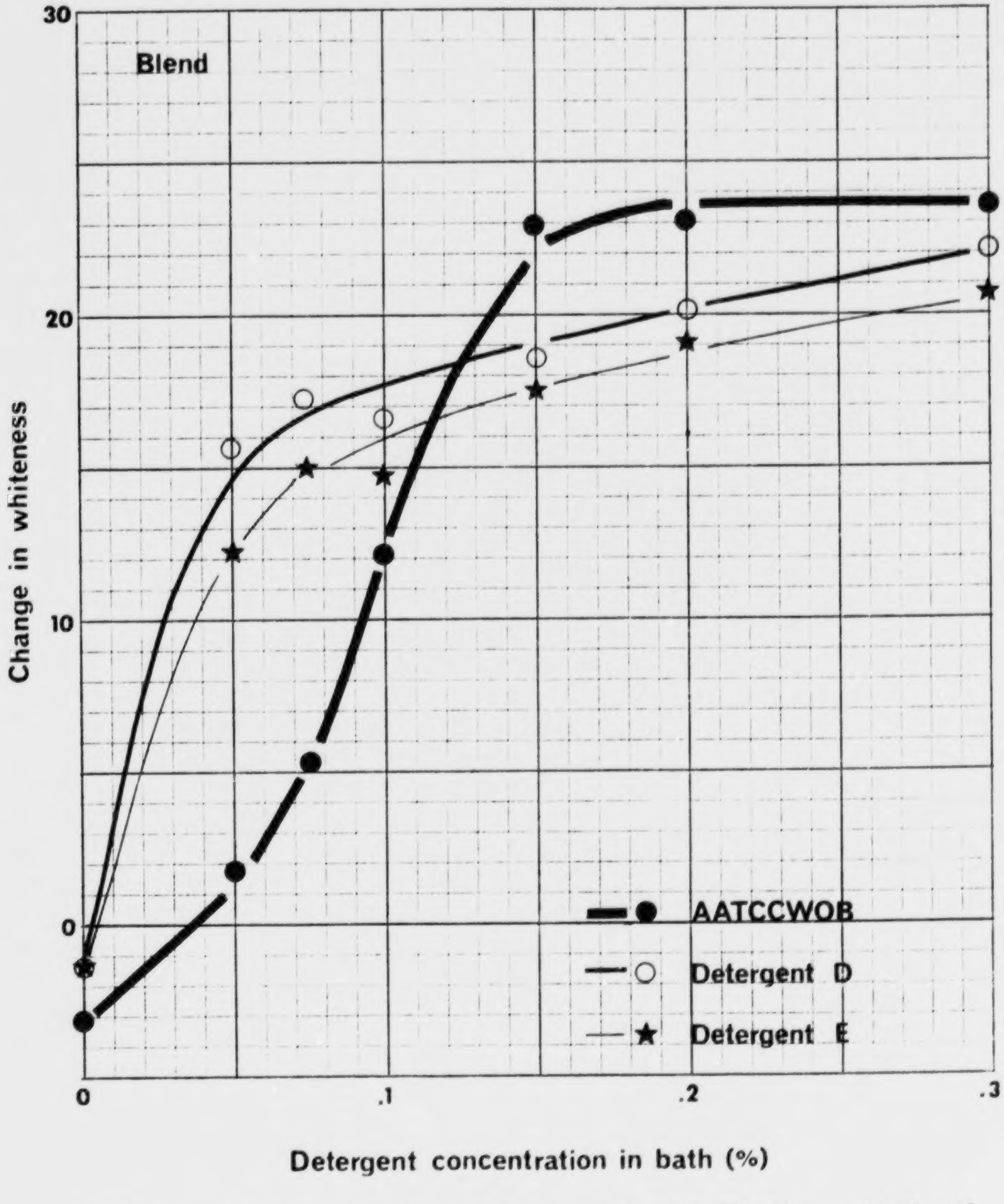

Figure 17. Detergency v. concentration. Items 104-855 (detergent D) and 96-782 (detergent E). Series refs. 252 (AATCCWOB) and 248. Colgate soil. 200 ppm water. Blend fabric.

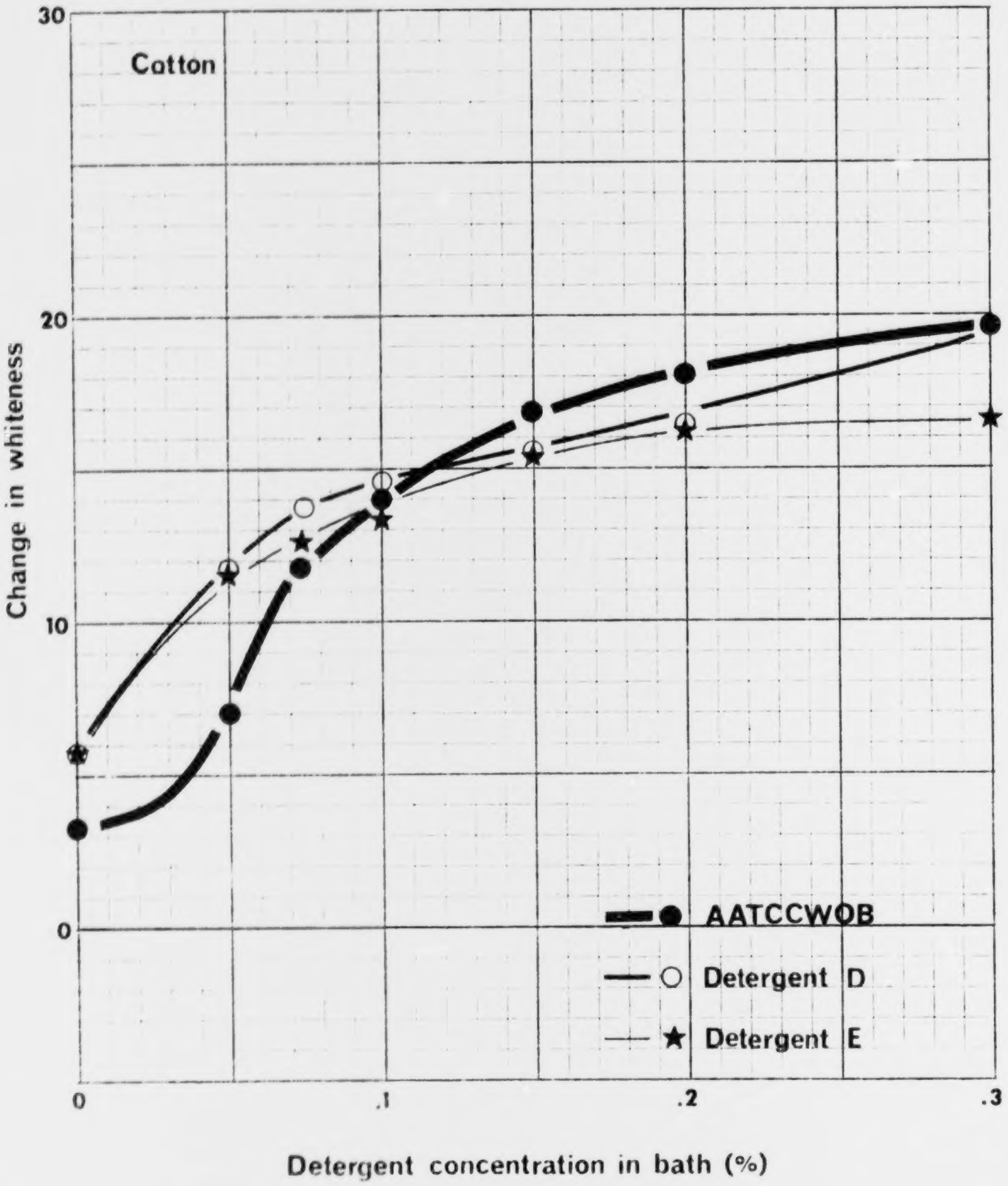

Figure 18. Detergency v. concentration. Items 104-855 (detergent D) and 96-782 (detergent E). Series refs. 252 (AATCCWOB) and 248. Colgate soil. 200 ppm water. Cotton.

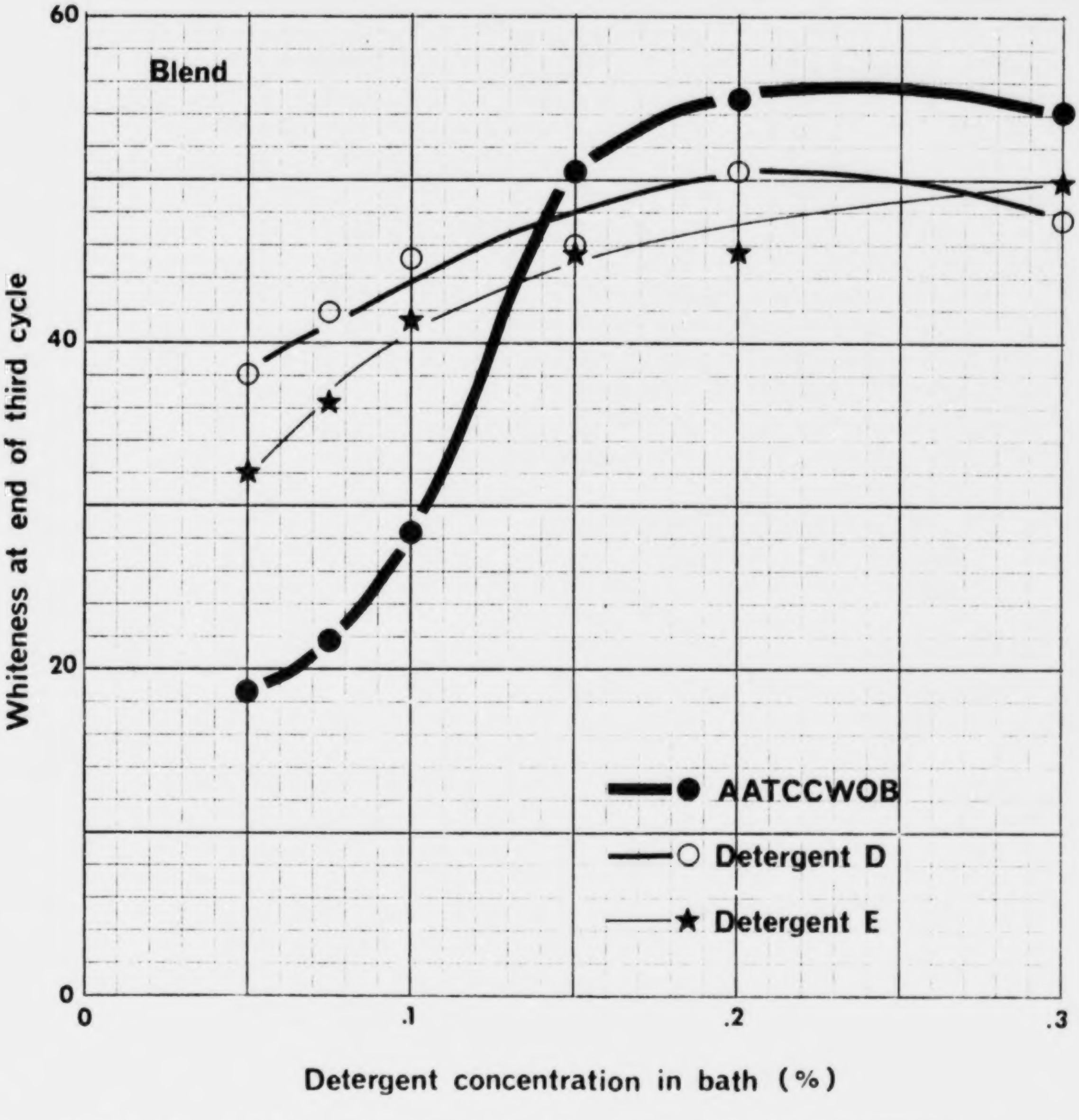

Figure 19. Detergency v. concentration. Items 104-855 (detergent D) and 96-782 (detergent E). Series refs. 253 and 254. Spangler multicycle. 200 ppm water. Blend fabric.

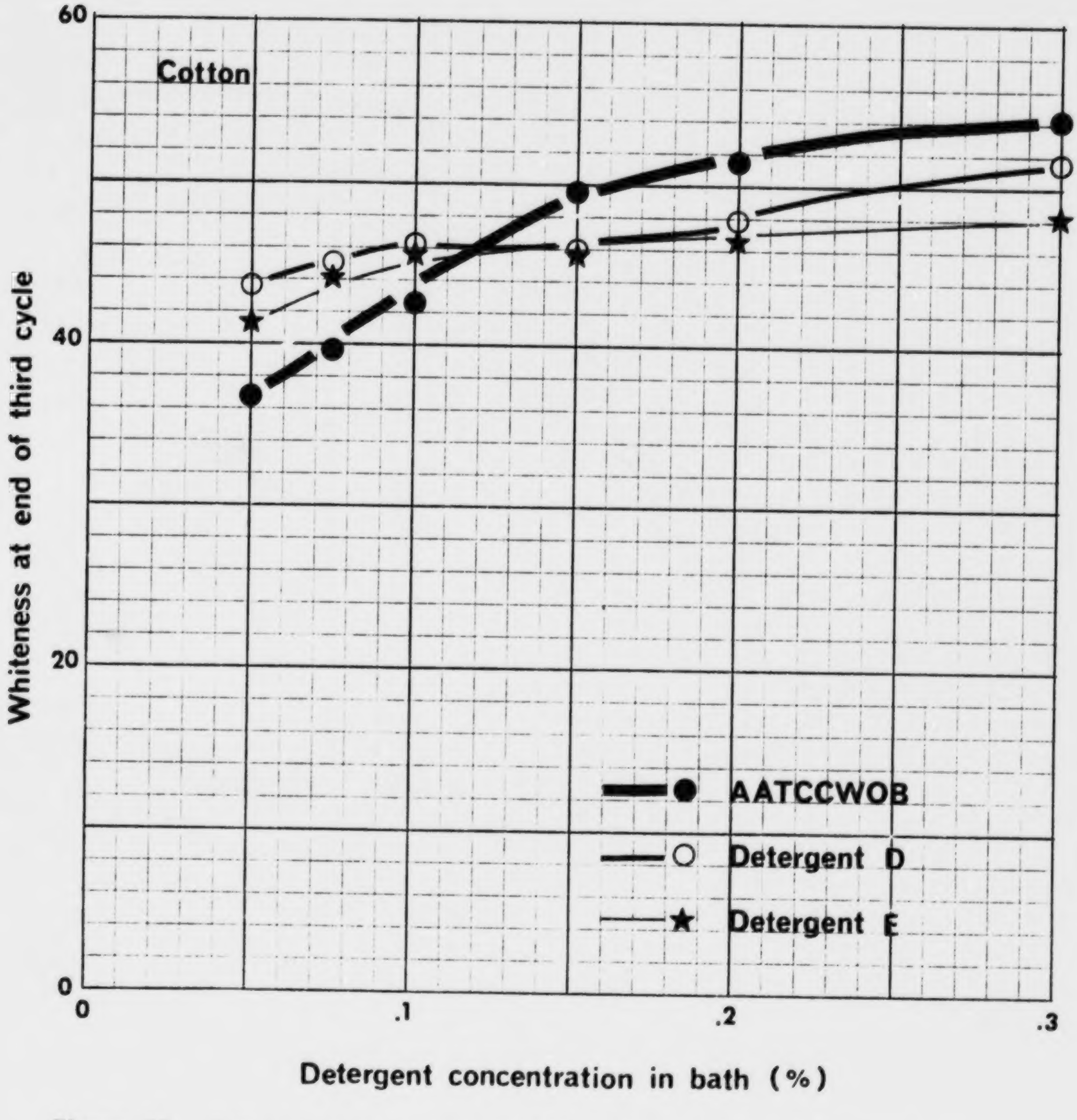

Figure 20. Detergency v. concentration. Items 104-855 (detergent D) and 96-782 (detergent E). Series refs. 253 and 254. Spangler multicycle. 200 ppm water. Cotton.

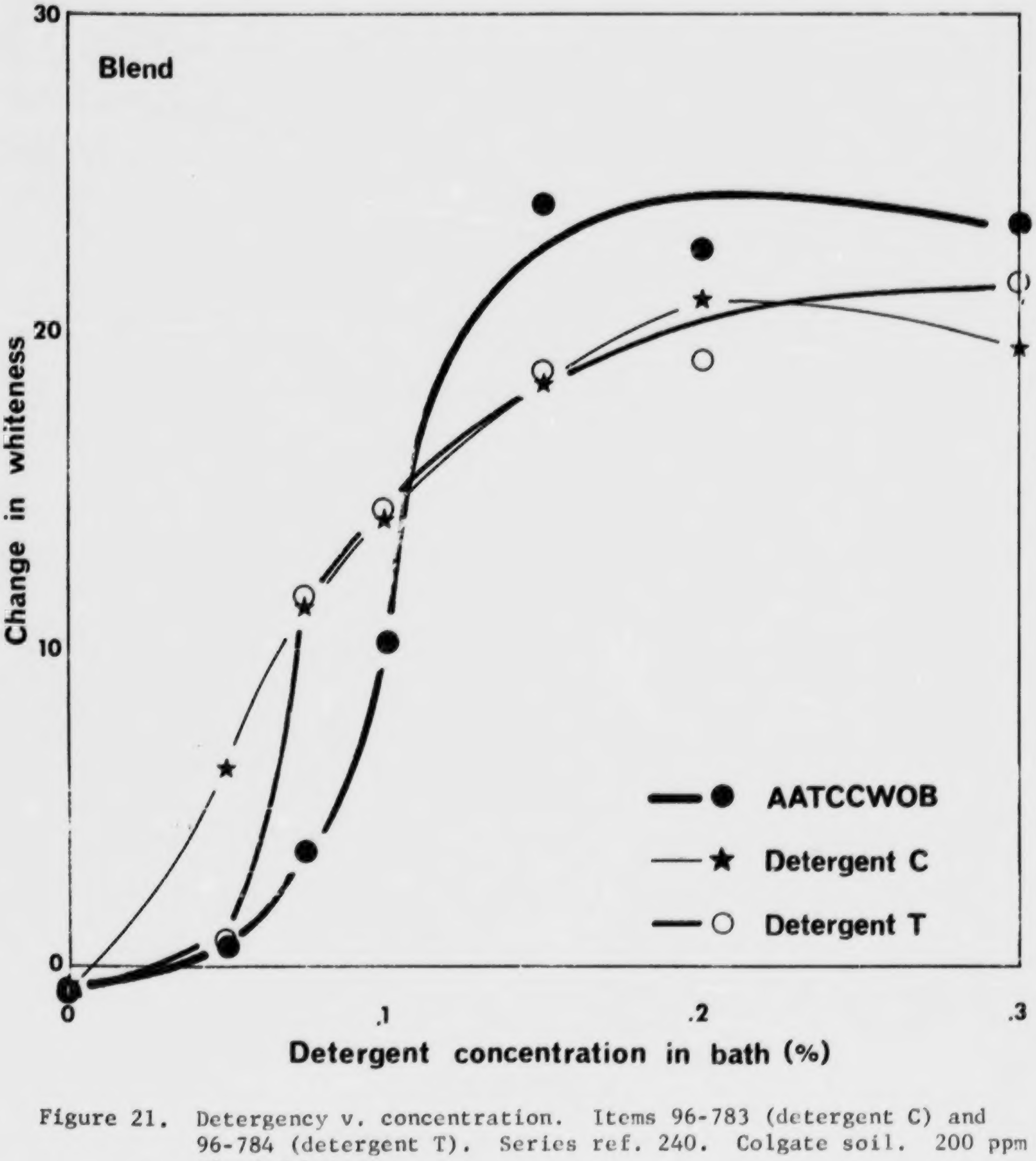

Figure 21. Detergency v. concentration. Items 96-783 (detergent C) and 96-784 (detergent T). Series ref. 240. Colgate soil. 200 ppm Blend fabric.

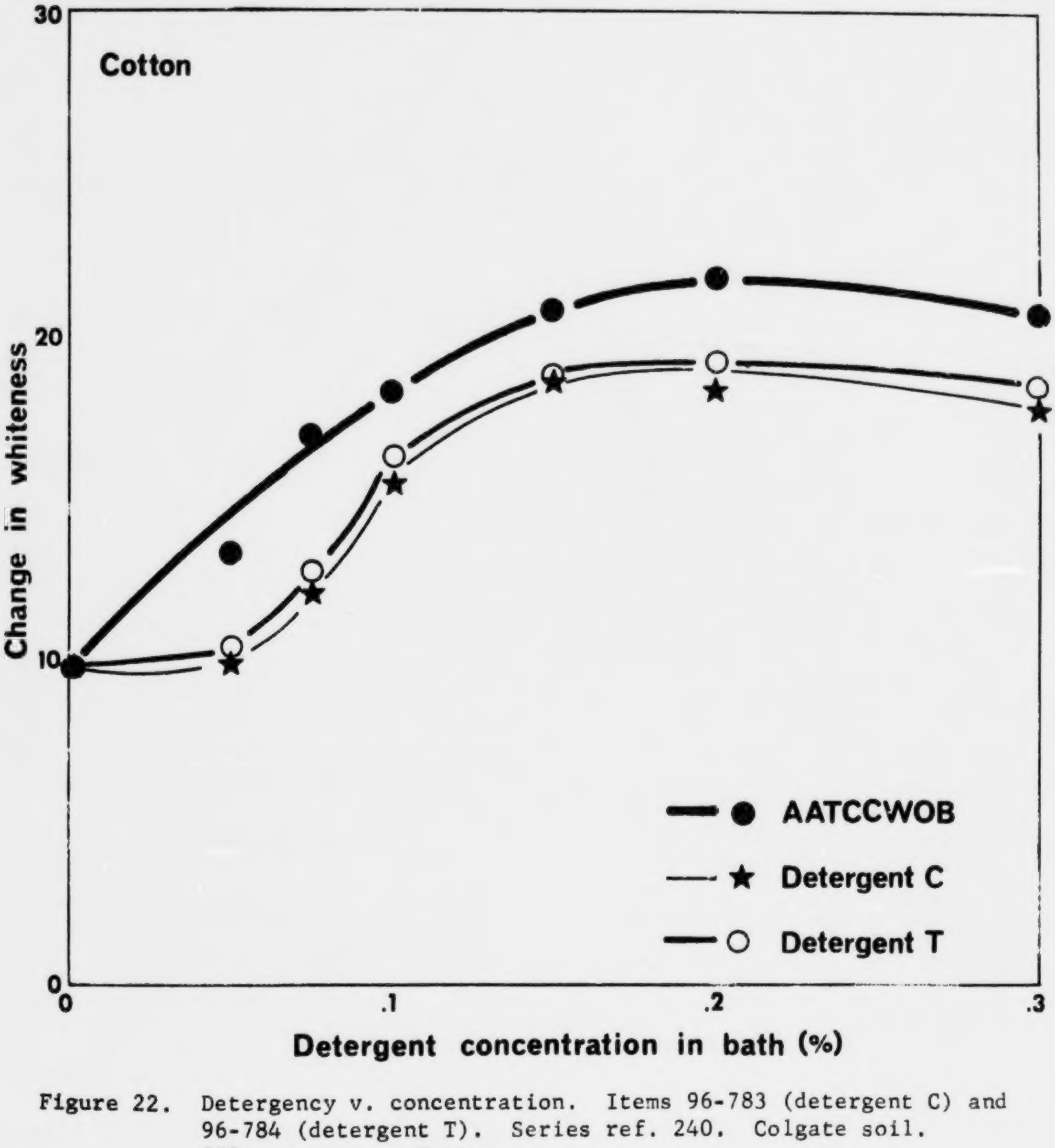

Figure 22. Detergency v. concentration. Items 96-783 (detergent C) and 96-784 (detergent T). Series ref. 240. Colgate soil. 200 ppm water. Cotton.

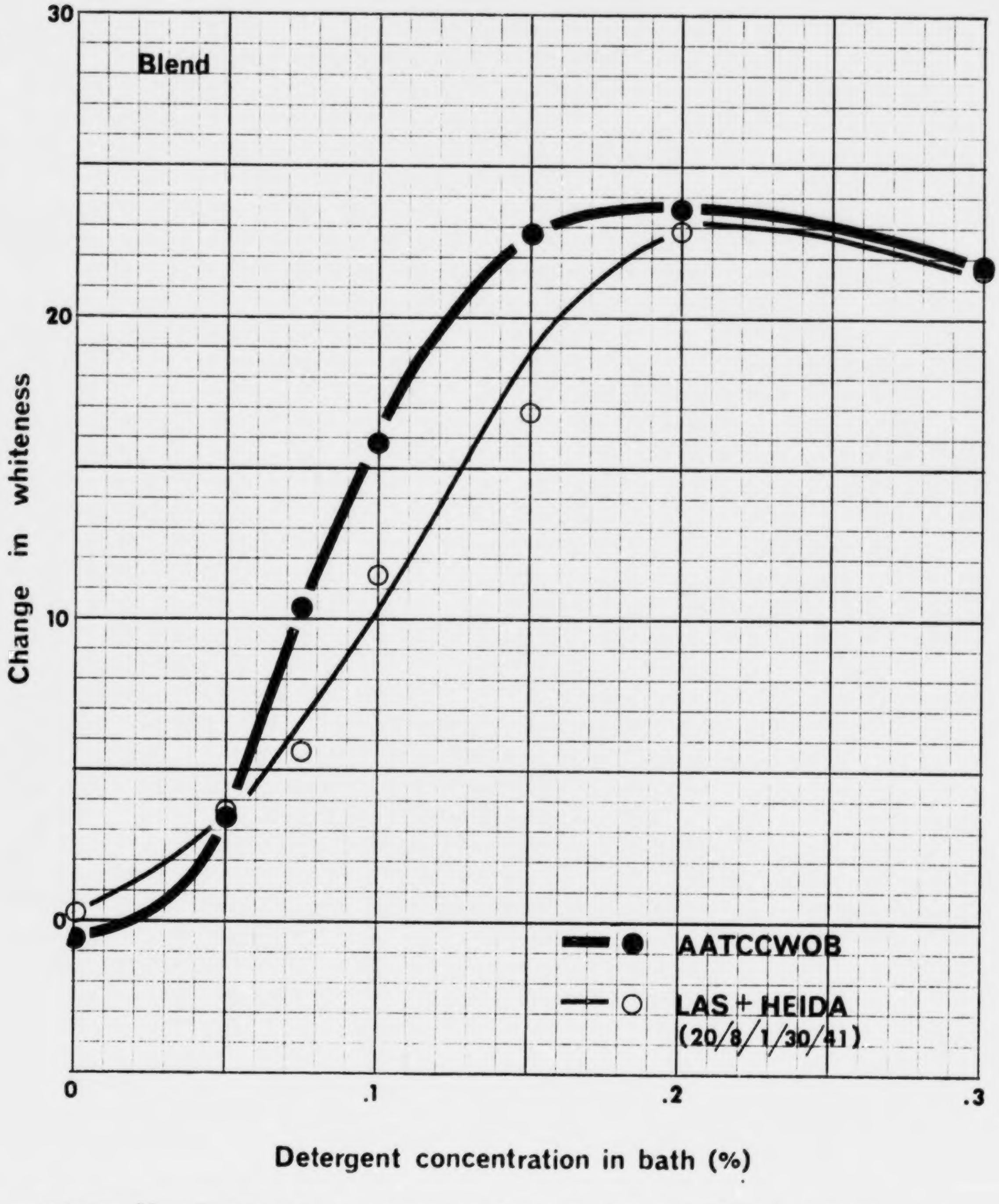

Figure 23. Detergency v. concentration. Series ref. 259 (AATCCWOB) 268 (HEIDA). Colgate soil. 200 ppm water. Blend fabric.

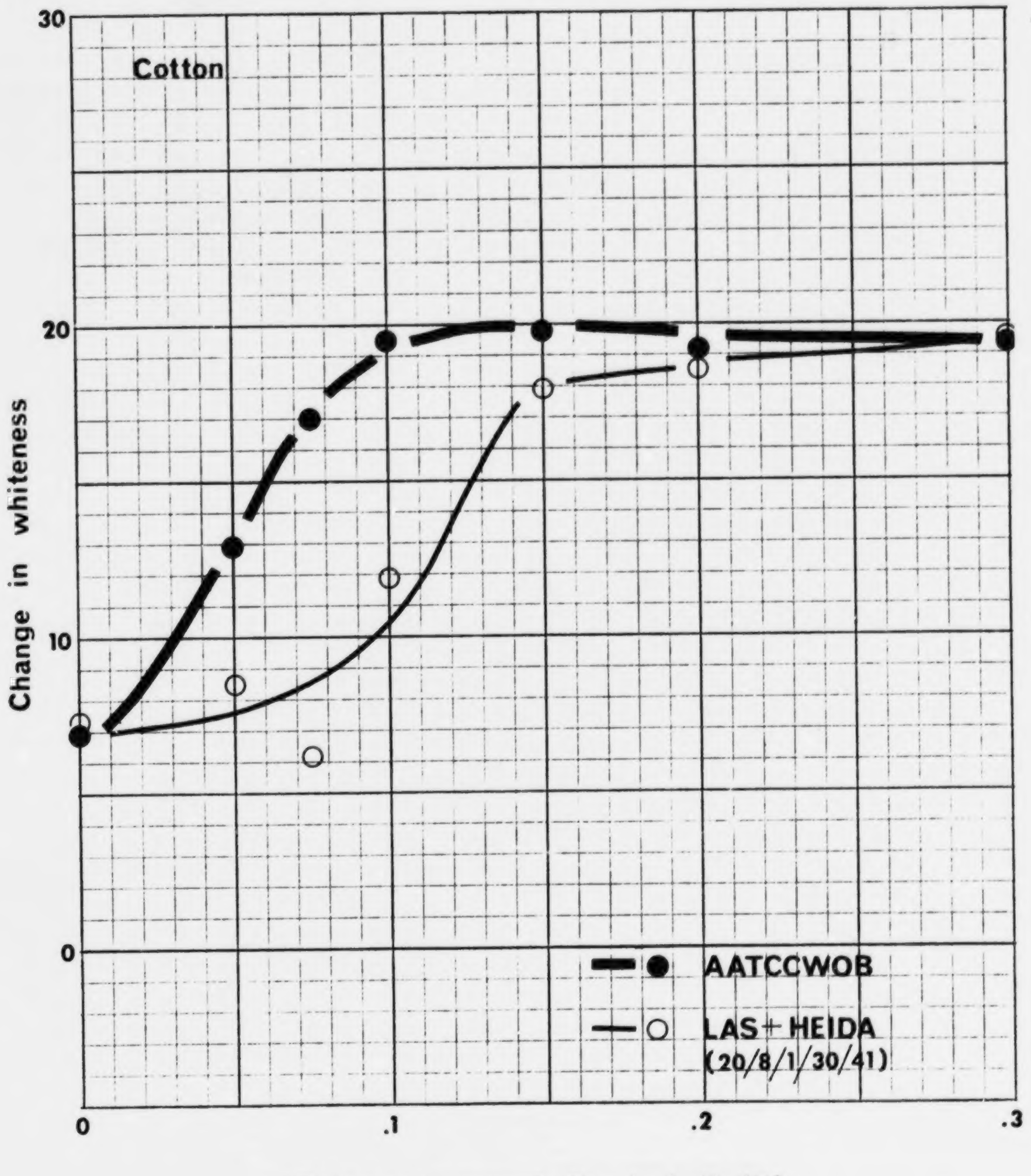

Figure 24. Detergency v. concentration. Series ref. 259 (AATCCWOB) 268 (HEIDA). Colgate soil. 200 ppm water. Cotton.

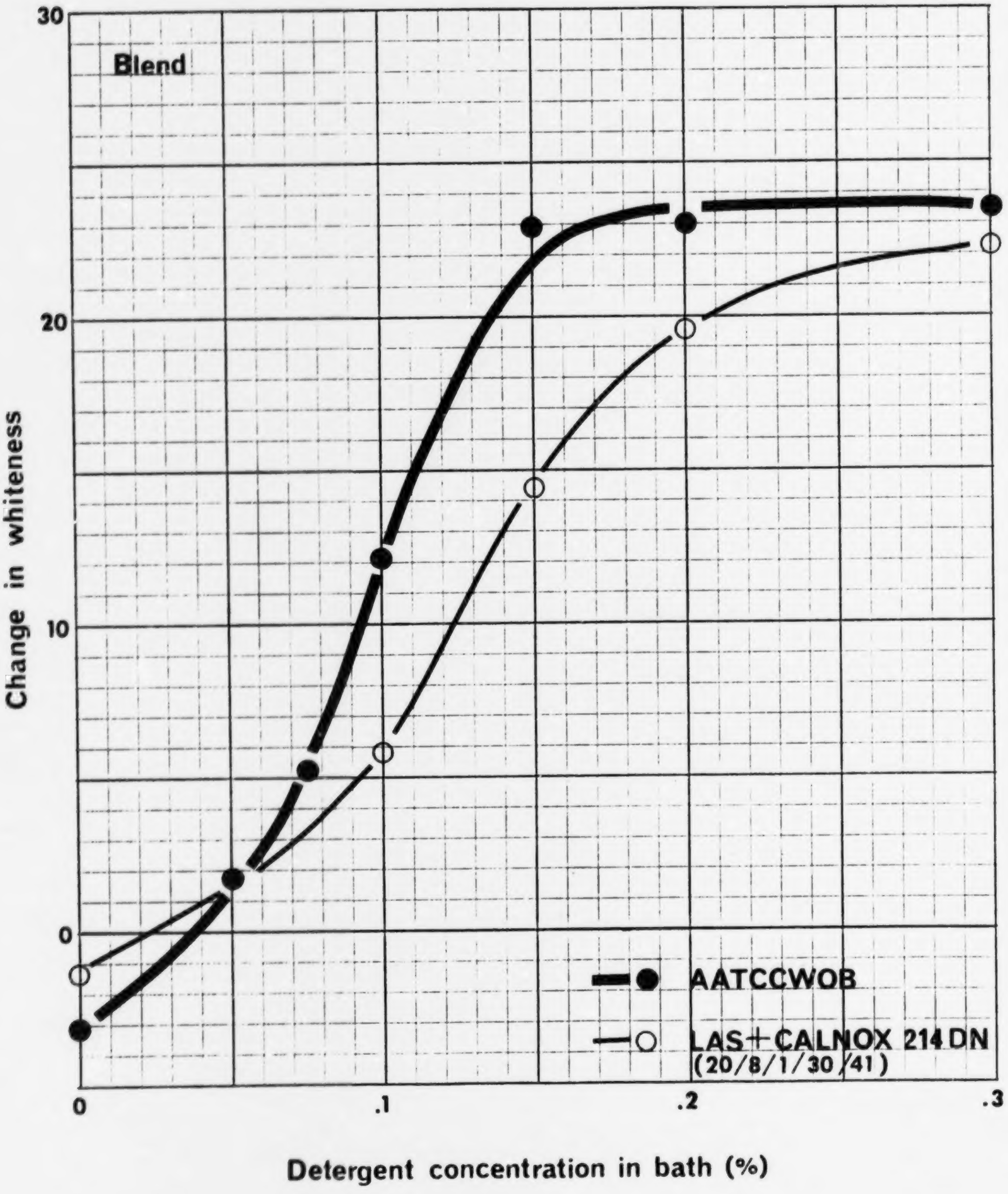

Figure 25. Detergency v. concentration. Item 100-823. Series ref. 252 (AATCCWOB) 255 (item 100-823). Colgate soil. 200 ppm water. Blend fabric.

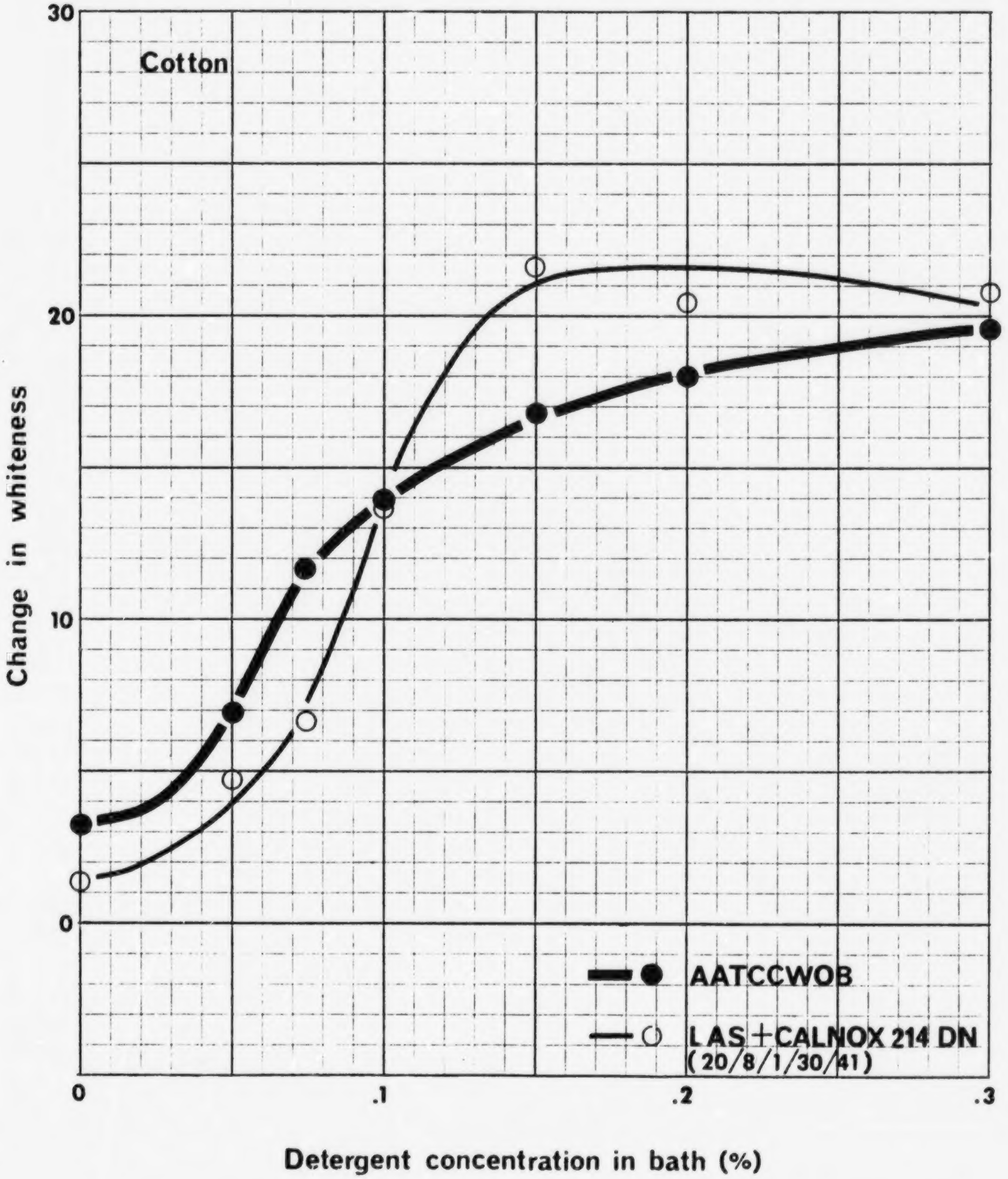

Figure 26. Detergency v. concentration. Item 100-823. Series ref. 252 (AATCCWOB) 255 (item 100-823). Colgate soil. 200 ppm water. Cotton.

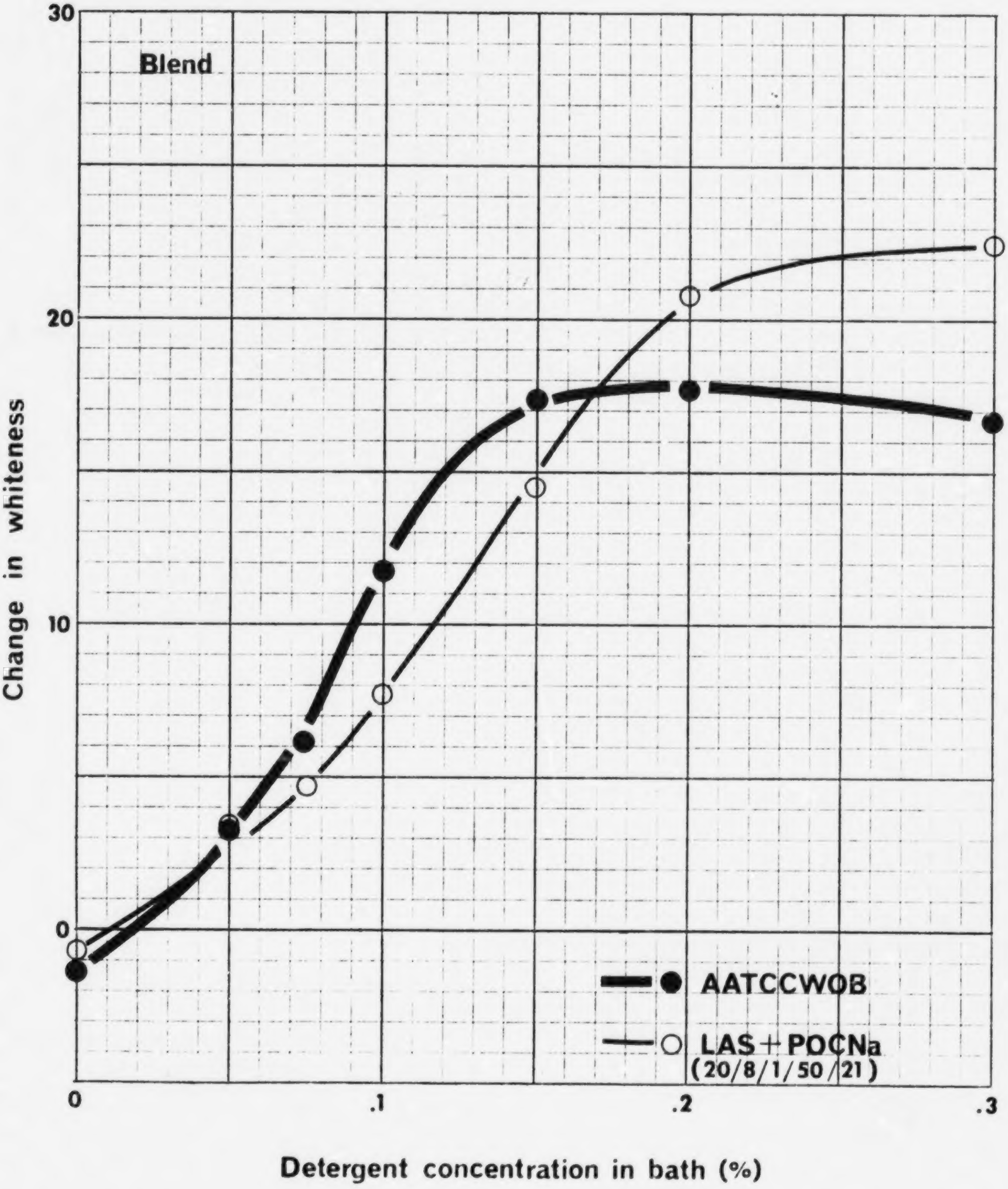

Figure 27. Detergency v. concentration. Item 104-860. Series ref. 259 (AATCCWOB) 257 (item 104-860). Colgate soil. 200 ppm water. Blend fabric.

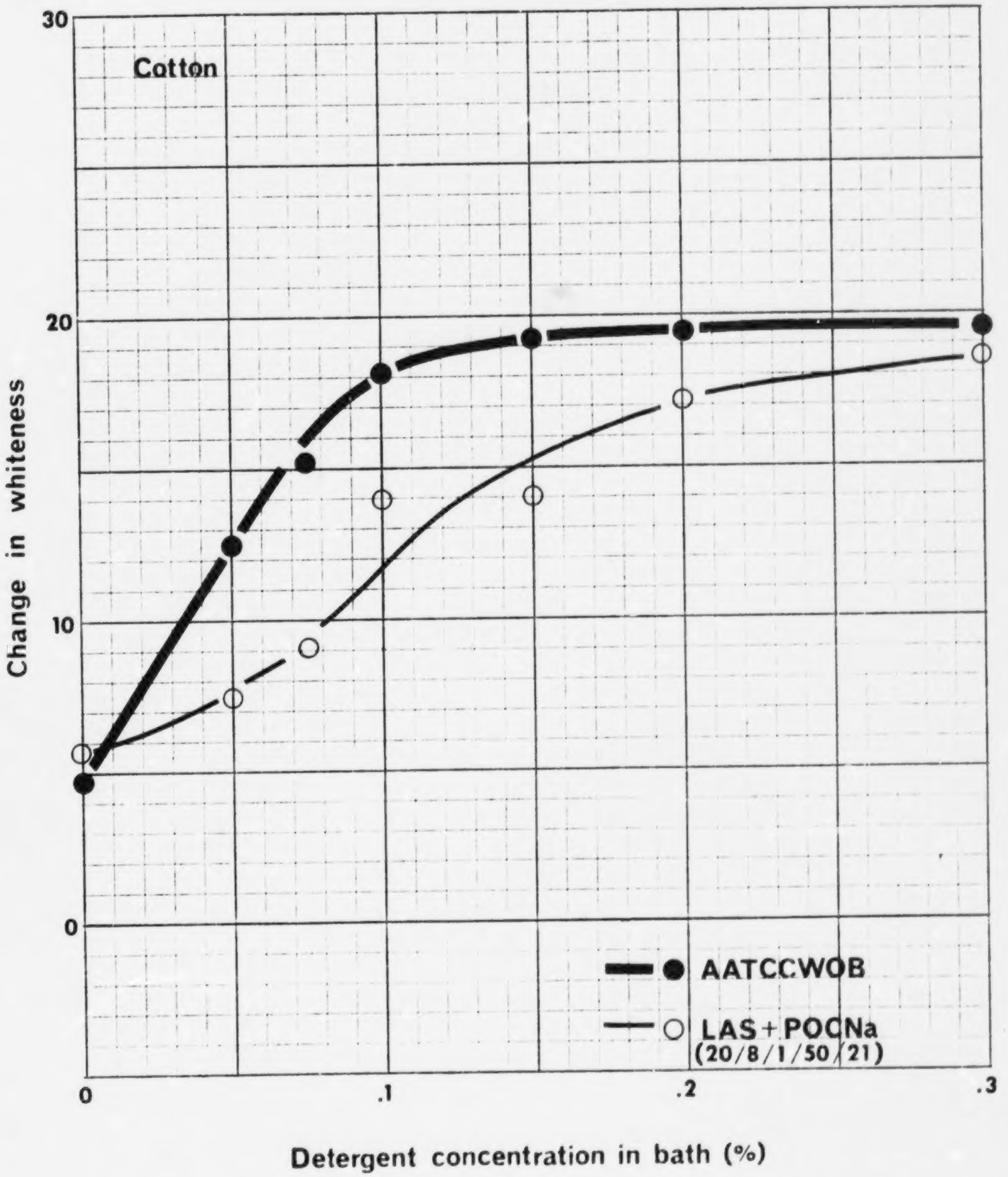

Figure 28. Detergency v. concentration. Item 104-860. Series ref. 259 (AATCCWOB) 257 (item 104-860). Colgate soil. 200 ppm water. Cotton.

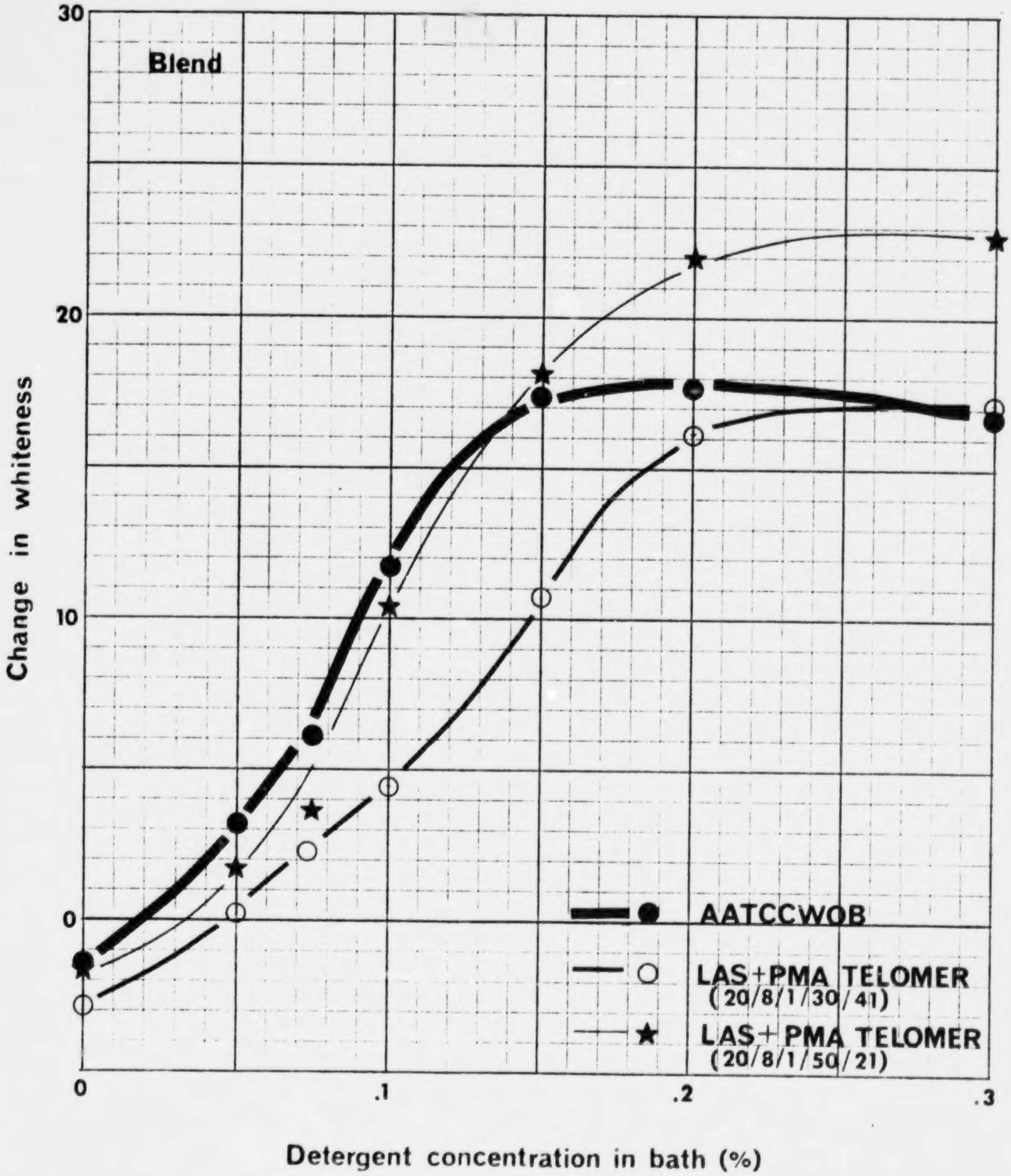

Figure 29. Detergency v. concentration. Item 106-866. Series refs. 258, 259, 260. Colgate soil. 200 ppm water. Blend fabric.

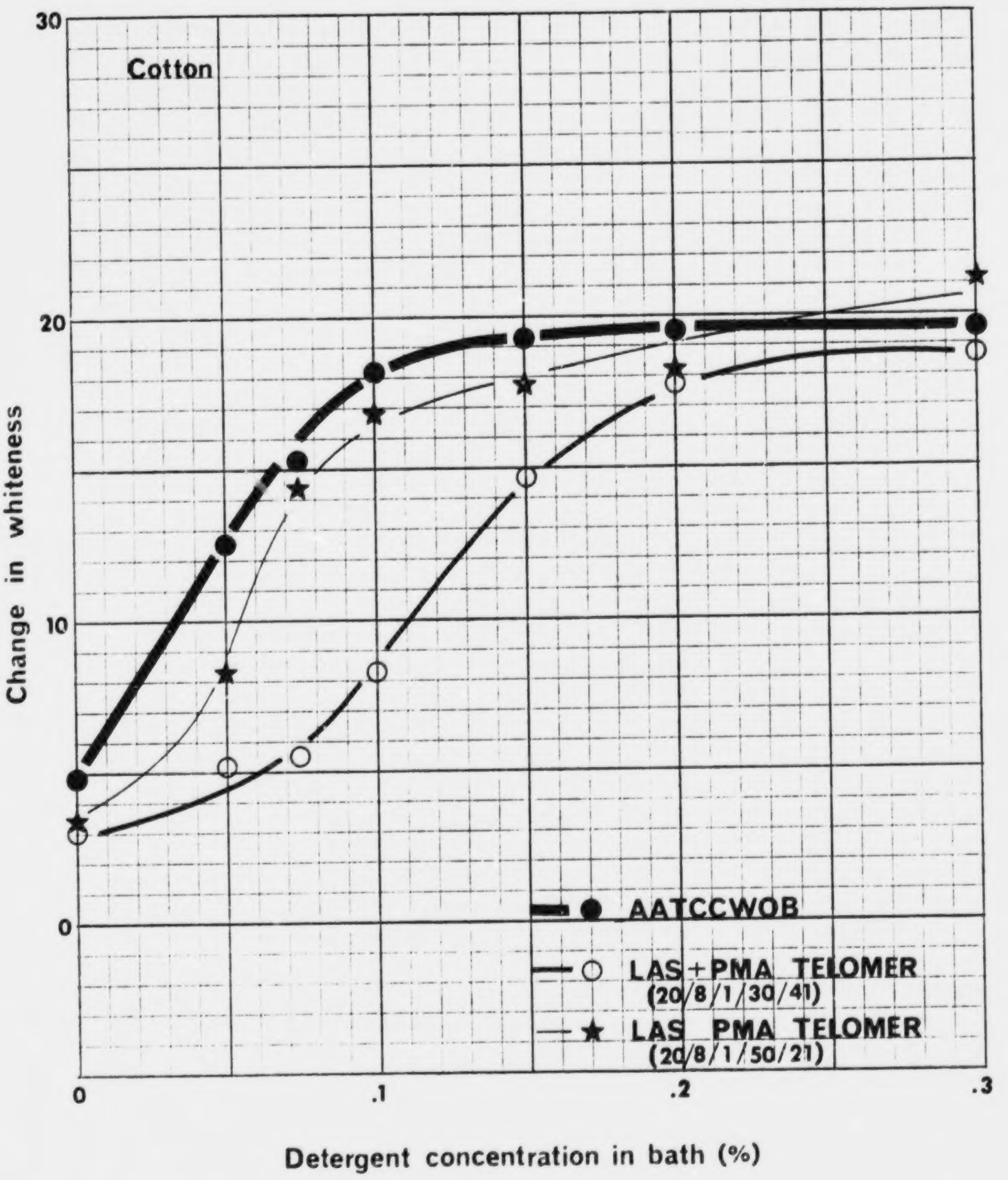

Figure 30. Detergency v. concentration. Item 106-866. Refs. 258, 259, 260. Colgate soil. 200 ppm water. Cotton.

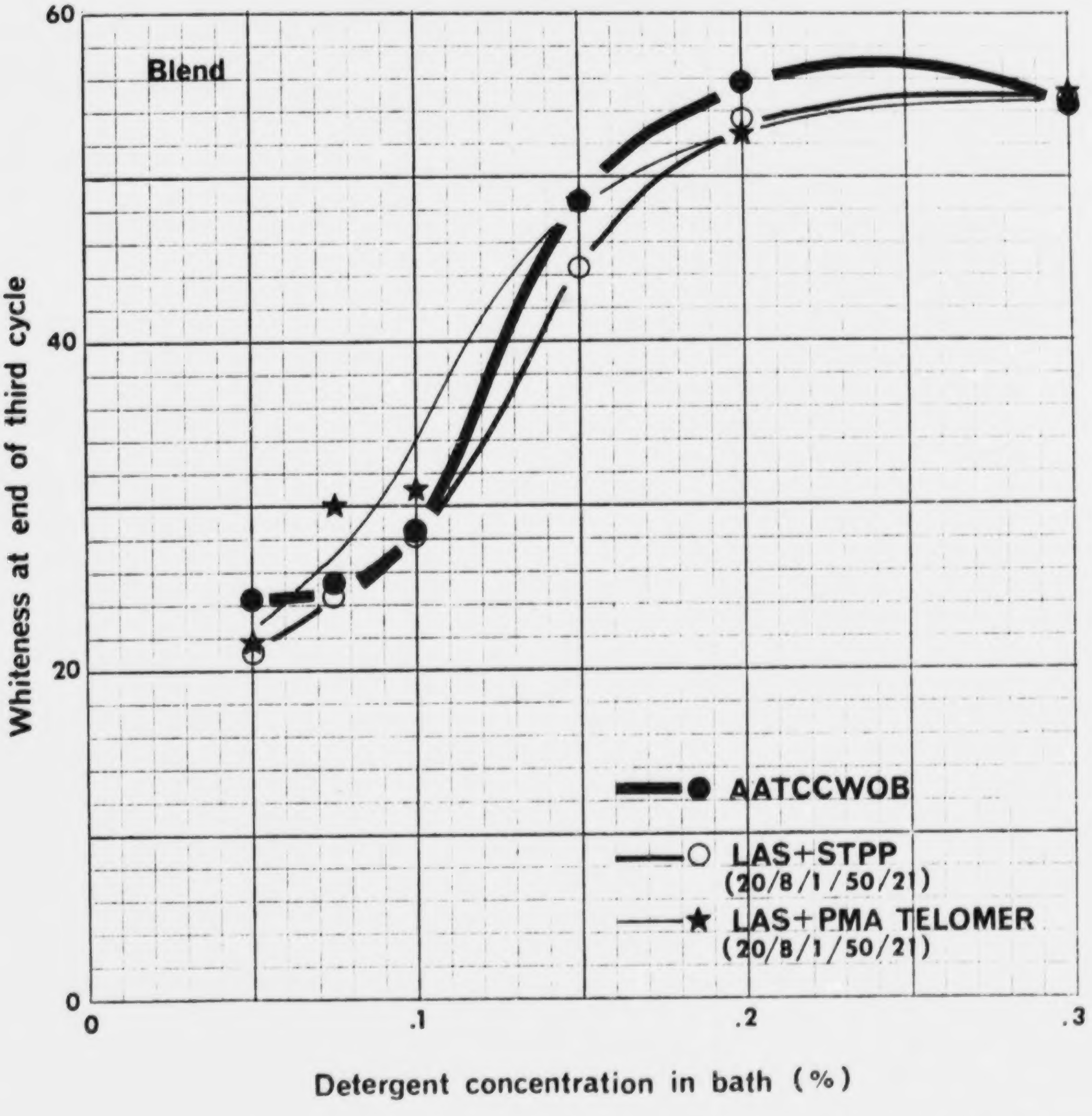

Figure 31. Detergency v. concentration. Item 106-866. Series ref. 267. Spangler multicycle. 200 ppm water. Blend fabric.

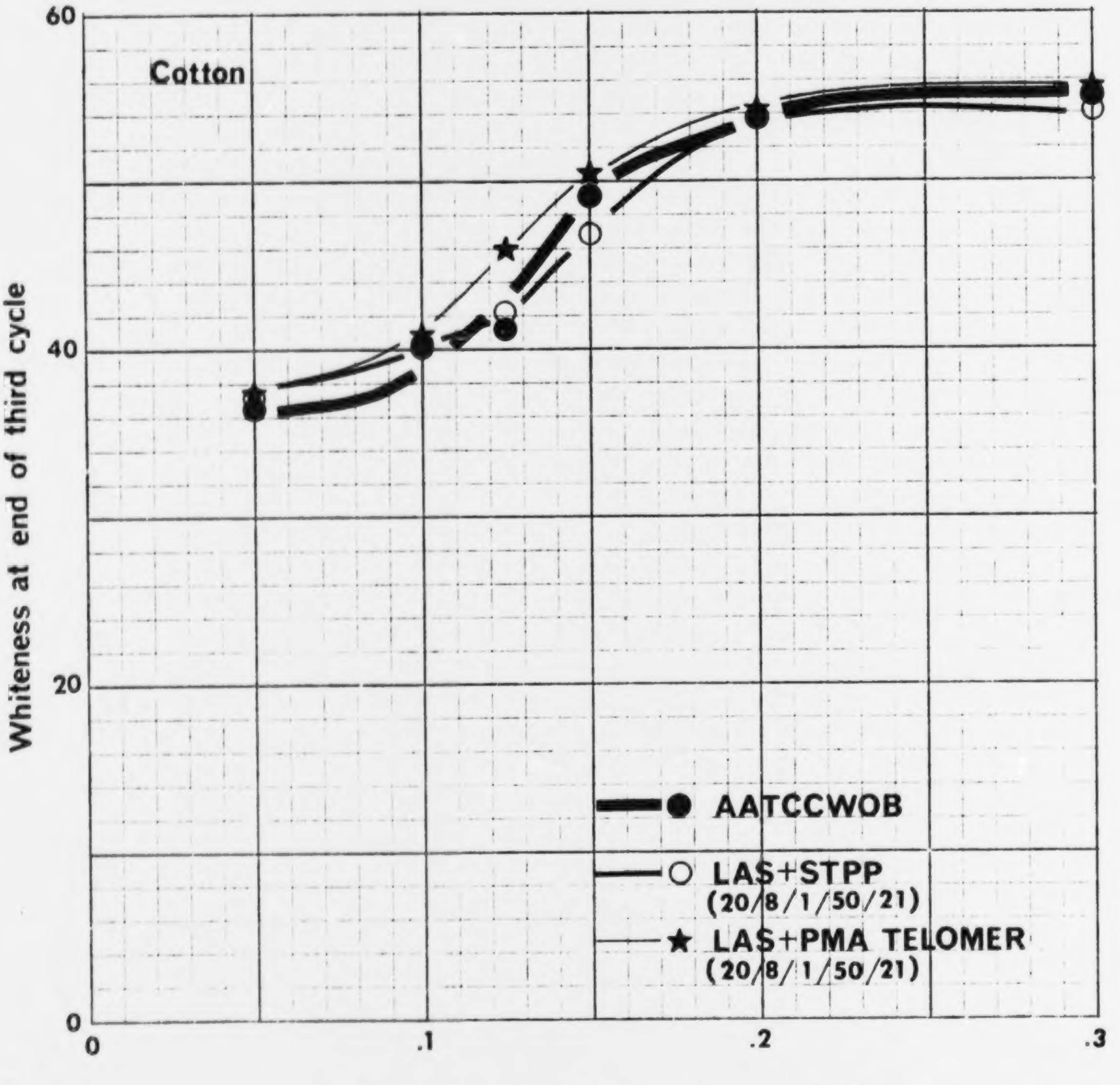

Figure 32. Detergency v. concentration. Item 106-866. Series ref. 267. Spangler multicycle. 200 ppm water. Cotton.

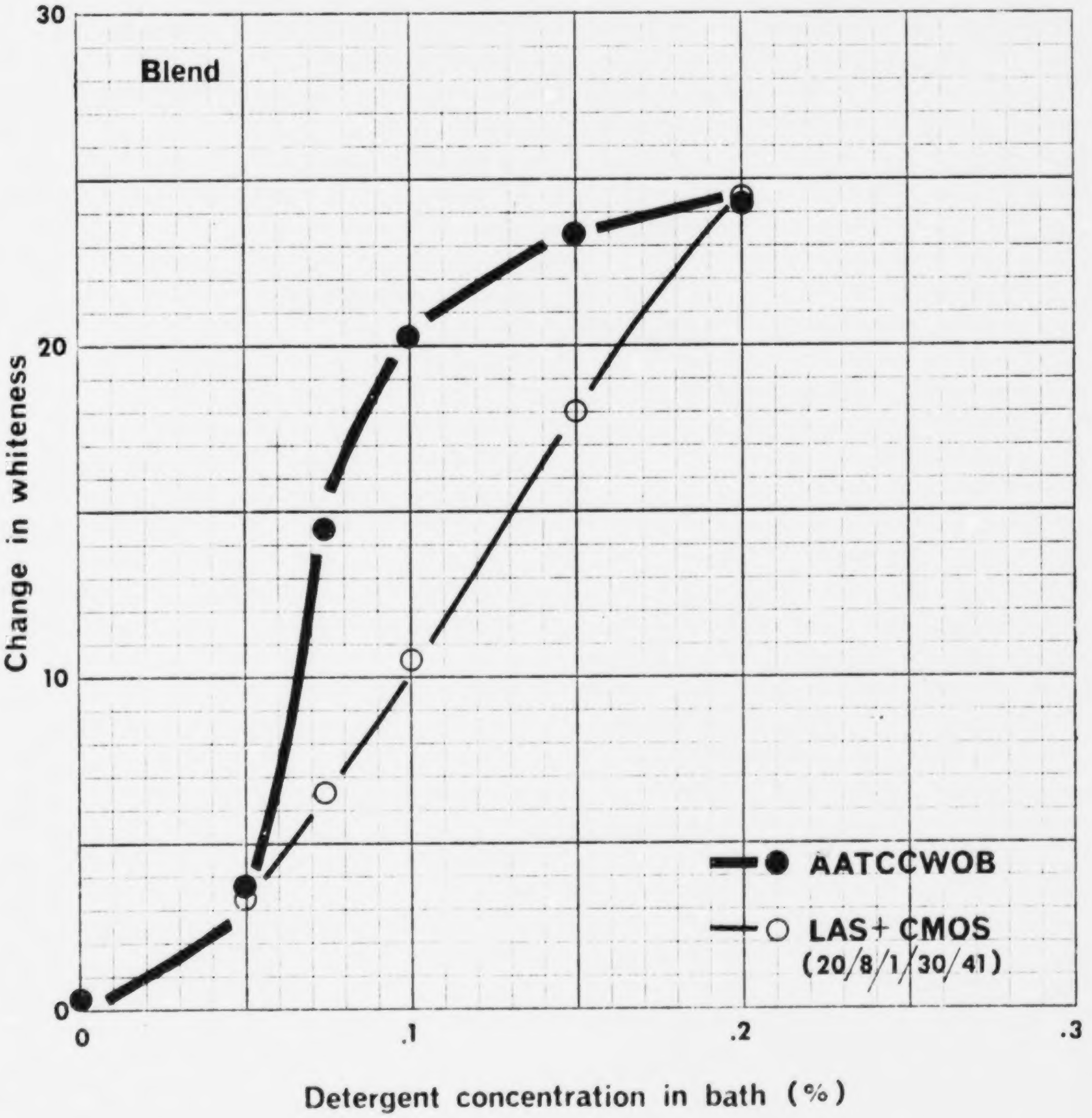

Figure 33. Detergency v. concentration. Item 80-647. Series ref. 243. Colgate soil. 200 ppm water. Blend fabric.

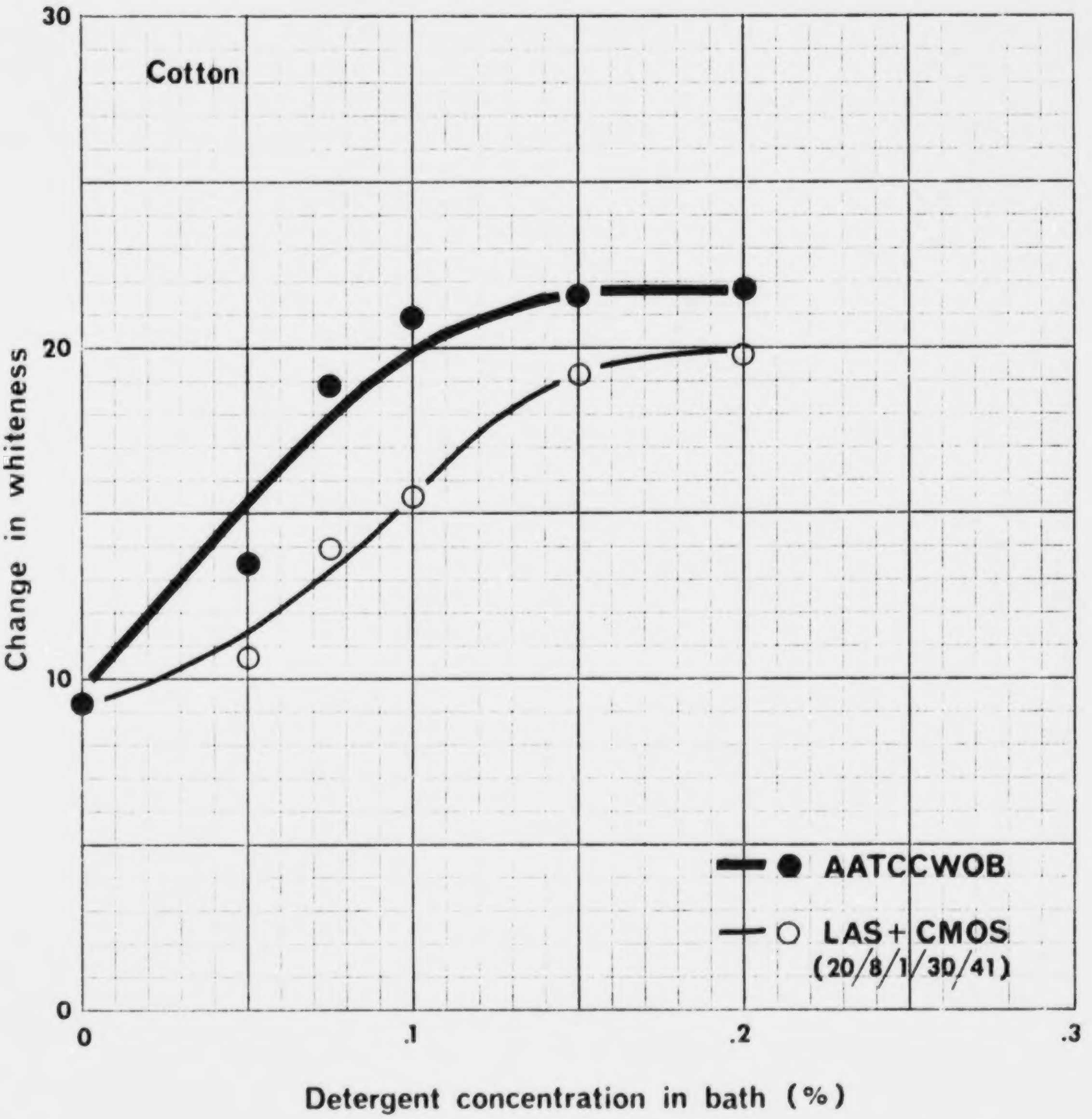

Figure 34. Detergency v. concentration. Item 80-647. Series ref. 243. Colgate soil. 200 ppm water. Cotton.

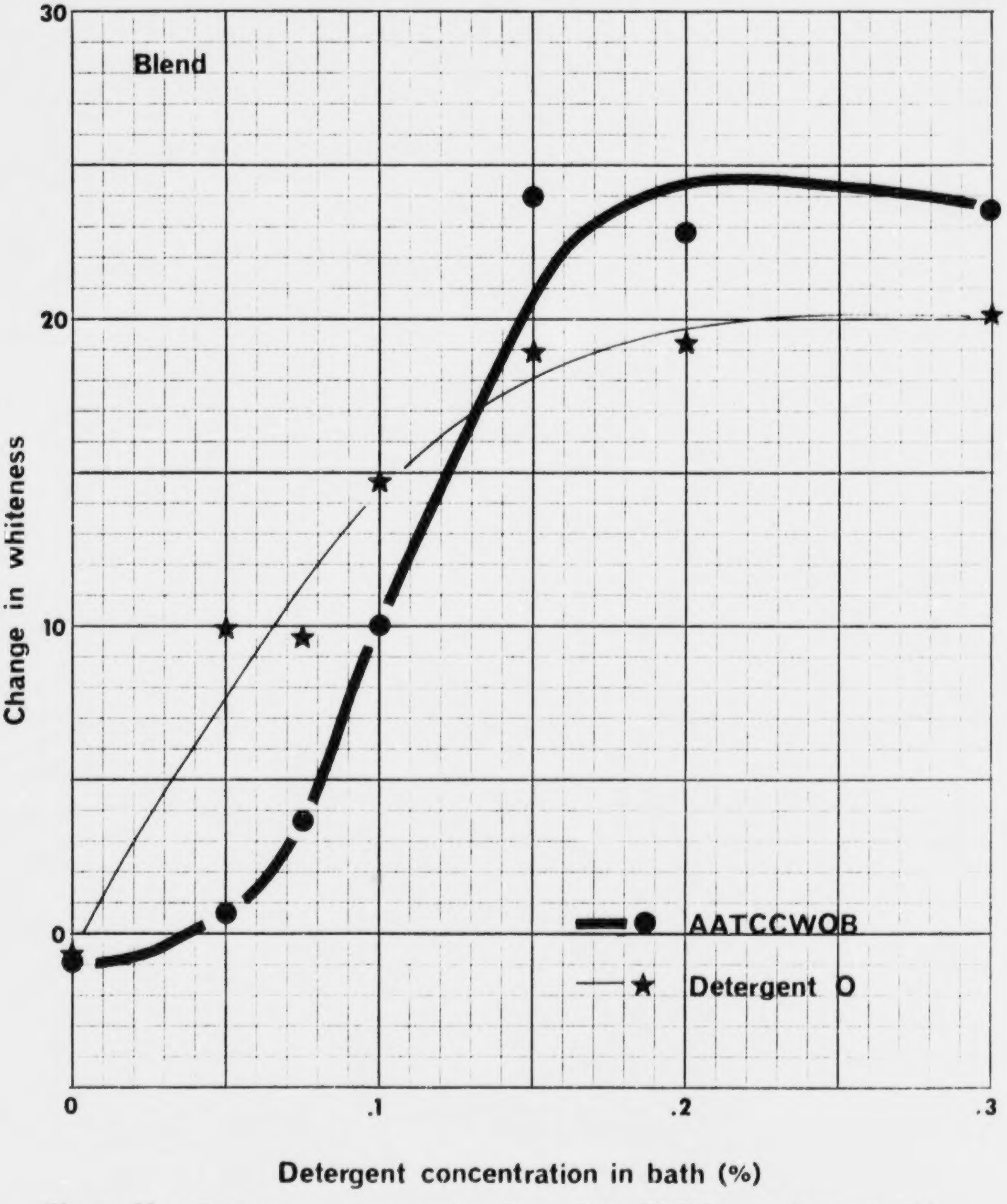

Figure 35. Detergency v. concentration. Item 90-279. Series ref. 240. Colgate soil. 200 ppm water. Blend fabric.

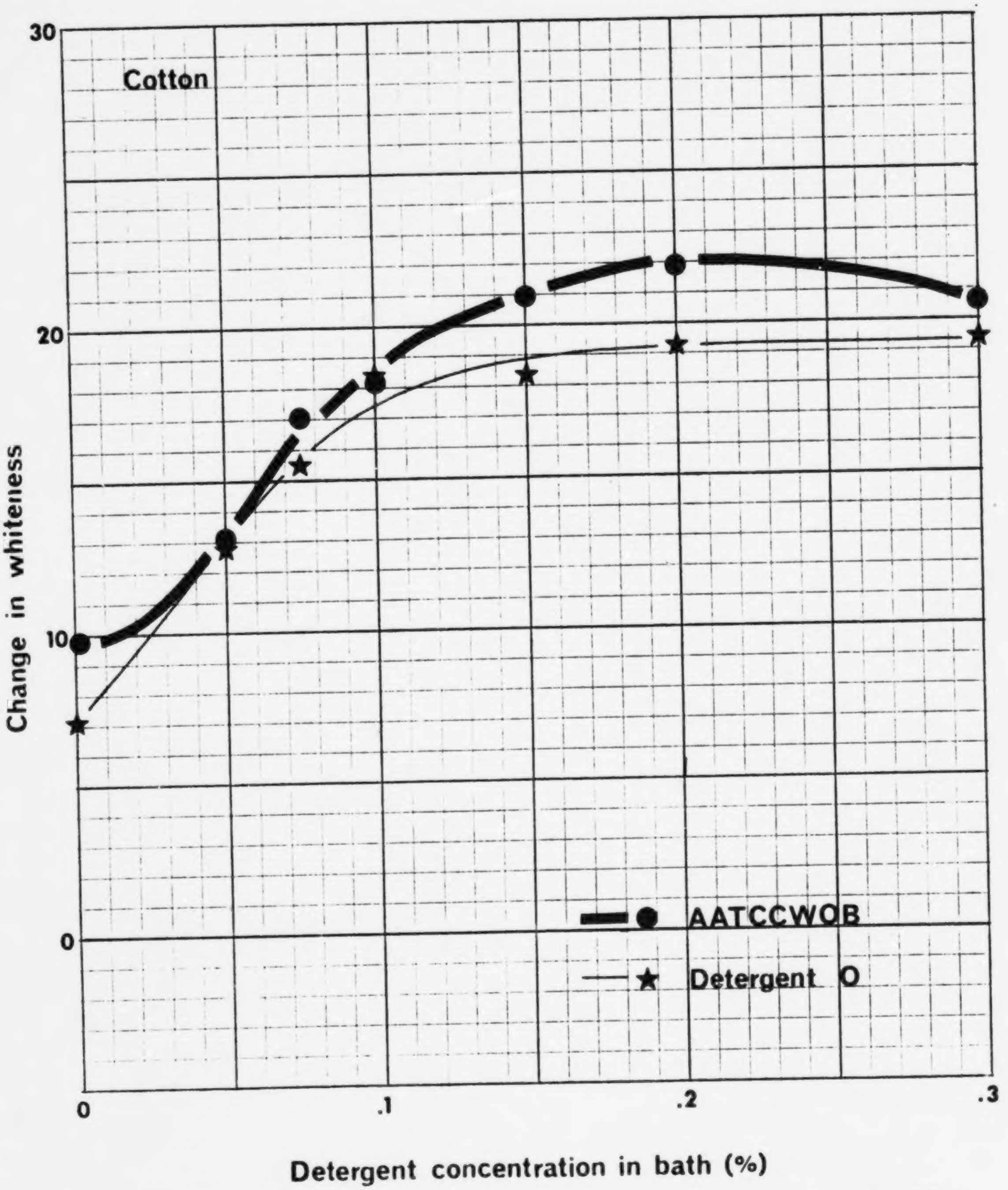

Figure 36. Detergency v. concentration. Item 90-279. Series ref. 240. Colgate soil. 200 ppm. Cotton.

APPENDIX A*

TEST METHODS, NON-LAUNDERING

I. BIODEGRADABILITY

A. Aerobic Biodegradability Tests

1. Affirm that the "active" organic surfactant is degraded aerobically under conditions of the Bunch-Chambers test procedure [R. L. Bunch and C. W. Chambers, J. Water Pollution Control Fed., 39 (2), 181 (1967)].

2. Test whether the proposed builder candidate (if it is organic) undergoes degradation in this static aerobic procedure.

    a. If the builder is not degraded, re-test the organic active in the presence of builder.

    b. If the builder does undergo aerobic biodegradation, re-determine the extent of degradation in the presence of the surfactant.

3. Test biodegradability of organic detergent formulation components other than the active surfactant and builder.

    a. Retest in presence of surfactant and builder to ascertain that there is no interference in degradation of any component. This is the test of the final formulation.

B. Biostimulation by Biodegradation Products

Test whether algal growth is stimulated (or inhibited) by the degradation products from A.3.a., above.

C. Toxicity of Biodegradation Products

Test the toxicity of the biodegradation products from full detergent formulations (A.3.a.).

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* For purposes of record the text of this appendix is reproduced verbatim from material in the contract proposal and specification. The protocols proposed and described herein are the ones subsequently used in performing the contract.

D. Anaerobic Biodegradability Tests

Test the complete detergent formulations as in A.3.a. except under anaerobic atmosphere in the culture flasks.

In the biodegradability tests, A above, settled sewage (from the Washington, D.C. area) or other inoculum specified by the Government will be used to inoculate solutions of test materials in BOD water containing yeast extract. The basal medium comprising BOD water (prepared according to "Standard Methods for Examination of Water and Waste Water", 12th ed. Amer. Pub. Health Assoc., New York, 1965) and yeast extract will be prepared beforehand and sterilized at 121°C for 15 minutes in an autoclave. The concentration and yeast will be selected consistent with the stimulation of microbial growth, but with minimal oxygen depletion; for most tests, yeast concentrations of 20 mg/l to 200 mg/l are satisfactory. The concentration of test material will be at least 20 mg/l in screening tests. Our standard for biodegradation of LAS type active will be dodecene-1 derived LAS and it must show 97.5% degradation (as determined by the methylene blue analytical method) in order for us to consider the results valid. Surfactants that are not methylene blue responsive will be analyzed by suitable chemical procedures when such are available. Measurements of foaming and/or surface tension will be used as auxiliary indications of surfactant content.

It is anticipated that analytical methods in the parts-per-million and parts-per-billion range will be lacking for some components. In such cases the primary test for biodegradability will be a standard BOD test. For this we use the method given in "Standard Methods for the Examination of Water and Waste Water", American Public Health Association, Inc. 12th ed. (1965) p. 415ff. This is modified to the extent that the dissolved oxygen (DO) is measured by the method and kit equipment described in Catalog #10, second revised edition of Hach Chemical Company, Ames, Iowa, p. 47ff. The BOD value, suitably corrected, is an index of the biodegradability of the substrate.

II. ALGAL STIMULATION

The basic test for algal stimulation used in this program was the Provisional Algal Assay Procedure ("PAAP test") issued by the Joint Industry-Government Task Force on Eutrophication, February, 1969, and its subsequently issued revisions. The test was made on four different organisms. Details are as follows:

A. Organisms Used:

Selenastrum capricornutum (green)
Microcystis aeruginosa (blue green)
Anabaena flos-aquae (blue green)
Navicula seminulum (diatom)

B. Physical Arrangements

Temperature - All algal work is carried out in a constant temperature room maintained at 24°C ± 0.5°C. Ambient temperature is recorded continuously and 7-day chart records are kept.

Lighting and shaking rates - All cultures are illuminated with cool-white fluorescent lamps. Light levels are checked weekly with a Gossen Tri-Lux foot-candle meter. *Navicula* and *Selenastrum* are grown on a laboratory-constructed shaker with a plexiglas platform, with the lights placed underneath this platform i.e. with "bottom-illumination" at 200 foot candles. For *Microcystis* and *Anabaena* a commercial (Eberbach Corporation) reciprocal shaker is used with overhead illumination at 150 foot candles. Both shakers are operated at 100 strokes/minute with a 2 inch throw.

C. Media for Carrying Stock Cultures

Three different stock culture media are used. All media are prepared with glass-distilled water. *Selenastrum capricornutum* and *Anabaena flos-aquae* are maintained on the medium of the published PAAP procedure. *Microcystis aeruginosa* does not grow well in the PAAP medium, and stock cultures are maintained in a solution described by Hughes, Gorham and Zehnder*. The major nutrients can be prepared as individual stock solutions, 1000X the final concentrations needed, so that 1.0 ml of each is used for each liter of medium. The final concentrations of major nutrients, in grams per liter of medium, are as follows: $NaNO_3$, 0.496; K_2HPO_4, 0.039; $MgSO_4 \cdot 7H_2O$, 0.075; $CaCl_2 \cdot 2H_2O$, 0.036; Na_2CO_3, 0.020; $Na_2SiO_3 \cdot 9H_2O$, 0.058; ferric citrate, 0.006; citric acid, 0.006; EDTA, 0.001. The final medium also contains 0.10 ml/liter of a "micronutrient" solution containing the following salt mixture (in grams/liter): H_3BO_3, 3.100; $MnSO_4 \cdot 4H_2O$, 2.230; $ZnSO_4 \cdot 7H_2O$, 0.287; $(NH_4)_6$-$Mo_7O_{24} \cdot 4H_2O$, 0.088; $Co(NO_3)_2 \cdot 6H_2O$, 0.146; $Na_2WO_4 \cdot 2H_2O$, 0.033; KBr, 0.119; KI, 0.083; $Cd(NO_3)_2 \cdot 4H_2O$, 0.154; $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$, 0.198; $VOSO_4 \cdot 2H_2O$, 0.020; and $Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$, 0.474. Although, in the original publication, autoclaving of this medium is recommended it was found that a precipitate is formed when this medium is autoclaved. The procedure has therefore been changed, and the medium is filter-sterilized (0.45 micron millipore filter), leaving out the ferric citrate and the "micronutrients" which are then added to the filtered medium. (Iron salts, and other heavy metal salts, tend to precipitate out on Millipore filters). The final pH of this medium is 9.5.

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*E. O. Hughes, P. R. Gorham, and A. Zehnder, "Toxicity of a Unialgal Culture of *Microcystis Aeruginosa*" Can. J. Microbiol. 4, 225-236 (1958).

Navicula seminulum is maintained in the "soft water" medium described in ASTM procedure D-2037-64T, "Evaluating Inhibitory Toxicity of Industrial Waste Waters." The final medium contains the following salts (in grams per liter): $Ca(NO_3)_2 \cdot 4H_2O$, 0.0761; K_2HPO_4, 0.0080; $MgSO_4$, 0.0400; KCl, 0.0200; $Na_2SiO_3 \cdot 9H_2O$, 0.3540; $CaCO_3$, 0.0100; and $NaHCO_3$, 0.0400. It also contains 4 ml/liter of soil extract (prepared by extracting 35g of "enriched garden soil" (commercial African Violet Soil) with 350g of boiling water and filtering through ashless filter paper). It also contains 1.0 ml/liter ferric citrate solution (1.820g ferric citrate plus 1.30g citric acid per liter); and 1.0 ml/liter of micrometabolite solution (this contains the following salts, in mg/liter: $ZnSO_4$, 20; $MnSO_4$, 14; $AlCl_3 \cdot 6H_2O$, 36; H_3BO_3, 20; LiCl, 10; and $CoCl_2 \cdot 6H_2O$, 10). The major nutrients are prepared as concentrated individual stock solutions. The micrometabolite solution is pre-mixed. The pH of the medium, before sterilization, ranges from 9.8 to 10.5, and is adjusted to pH 9.5 with HCl. The final solution is sterilized by autoclaving at 20 psi for 20 minutes.

D. Experimental (Test) Media

For Anabaena, test media and stock culture media are identical; for Selenastrum the test media are half the concentration of the stock media. In each case, after addition of the test material (but before addition of culture inocula) the pH is readjusted to 7.5 by the addition of either 1N NaOH or 1N HCl (usually, one or two drops per liter of medium).

The test medium for Micorcystis is also the standard PAAP medium. However, before use, Microcystis maintained in the "rich" stock medium is subcultured twice, for 7 days each time, in the PAAP medium. This is necessary to reduce the effects of nutrient carry-over.

The ASTM medium used for Navicula stock cultures was designed for toxicity testing rather than for evaluating biostimulatory potential of materials, and is a "rich" medium. Therefore it must be diluted if the addition of biostimulatory materials is to show any effect. The test medium used at present contains one-fourth (1/4) the concentration of all constitutents of the stock medium, except for sodium metasilicate; the silicate concentration is kept at the original level. The pH of this medium is adjusted to 9.5.

Before inoculation into test media, cells are centrifuged and washed, essentially as described in the PAAP protocols, except that they are washed with test medium rather than with distilled water. The volume of inoculum (except for Anabaena) is adjusted so that, at the start of the experiment, cell concentrations will be as follows: Selenastrum, 1×10^3/ml; Microcystis, 5×10^4/ml; and Navicula, 4×10^4/ml.

Anabaena, a chain forming organism, is not counted. A uniform suspension is prepared (30 seconds in sterile Waring Blender) and aliquots are dispensed into test flasks. A larger aliquot is filtered through a 0.45μ millipore filter and dried for determination of biomass. (When 100 ml of 7-day stock culture are centrifuged, and the pellet resuspended in 100 ml of medium, 50 ml of suspension yield approximately 5 mg of dried material.) Generally, 2.0 ml aliquots are used, leading to a "dry weight" level of 2×10^{-3} mg/ml.

For any of the organisms the concentration of test material added to the test medium can vary widely, and the choice of a concentration level should be guided by the expected action of the test material and by its expected concentration in the field. It can advantageously be set between .1 and 10.0 ppm (mg/liter) in most cases.

E. Methods for Evaluating Growth

Three different methods for evaluating algal growth are used: (a) direct cell count, (b) absorbance at 450 and 600 nm; and (c) biomass (dry weight).

The last method, gravimetric determination of dry weight, is used only with Anabaena. Matched weight, 47 mm 0.45μ Millipore filters are used in a "double" assembly; that is, both filters of the matched pair are placed in the filter holder, and the entire culture filtered. Each filter is dried under identical conditions and weighed; the difference in weight between the two filters is taken as the dry weight of Anabaena in the volume filtered. During this "screening" stage 7-day cultures of Anabaena are harvested and weighed, thus, this is a single-point estimation of total growth, not an estimation of rate.

Navicula growth also is estimated by total growth during a fixed time period (10 days or more) rather than by rate. Since Navicula tends to stick to the walls of the flasks, and to form gelatinous masses, all flasks are carefully scraped and the contents mixed rapidly in a Waring Blender (as recommended in the ASTM procedure).

Growth of both Selenastrum and Microcystis is estimated both by total growth, and by growth rate. Since these algae are unicellular and do not tend to clump or adhere to vessel walls, small aliquots can be removed periodically throughout the time of incubation, and increases in cell numbers can be followed readily. These two organisms are grown in 300 ml Nephelo flasks (Bellco Glass, Incorporated, Vineland, New Jersey, Catalog No. 524) so that absorbance of the culture can be measured with a B&L Spectronic 20 directly in the flask, without removal of aliquots. For each experiment, 5 control flasks and 5 flasks supplemented with test compound are used.

A Coulter Counter, Model Z_BI, equipped with a Mean Cell Volume/Hematocrit attachment is used for cell counts and determination of mean cell volumes. The same 70μ aperture can be used for each of the organisms counted. Isoton, a commercially available electrolyte solution, is used as the diluent.

III. AQUATIC TOXICITY

Two types of test were used in the program, referred to for brevity as the acute or screening test and chronic test. The chronic test requiring a minimum of two months for fish and varying times for other organisms, was ultimately used on only two formulations. The screening test involves a 96 hour exposure, and was used, as its name implies, to screen out candidate materials that are definitely unsatisfactory with regard to aquatic toxicity. Three test organisms are used in our present screening procedure: a fish, a gilled snail, and a diatom. In the chronic tests it is planned to use the following organisms:

1. Two diatoms (algae)--desirable food species, one typical of lakes, the other typical of streams.
2. Insects--a genus and, if possible, a species typical of as many types of streams as possible.
3. Two snails--a genus, and, if possible, species typical of many types of lakes and streams as possible; a pulmonate and a gill breather.
4. Crustacea--a genus and species typically found in lakes.
5. Fish--catfish or suckers, algae and detritus feeders.
6. Fish--sunfish species found in many types of lakes and streams.

A. General Acute Testing Procedures

The following general considerations apply to acute testing procedures:

1. All acute bioassays will be conducted using continuous flow rather than static techniques. The continuous flow method insures that waste products of metabolism do not build up in the test container, decrease the chances of test material adhering to the sides of the container, allow minimum modification of the environment by the test organism, eliminates the need for any aeration in the test chamber since aerated dilution water is constantly flowing, and insures accurate monitoring of test concentrations throughout the test period. All these factors, if not controlled, result in inaccurate and unreliable test results.

2. All acute bioassay tests will be conducted over a 96-hour test period with mortality readings taken every 24 hours. The 96-hour exposure period is now the accepted acute exposure time by most authorities. Shorter exposure times very often produce a distorted picture because of possible lag of toxic effect.

3. A minimum of five concentrations plus control will be used for each test material. The concentrations will be set up in a logarithmic series as outlined in Standard Methods. This logarithmic series has proved to be most efficient over the years in determining critical toxic concentrations. Partial mortality of the test organisms must be obtained at each of two concentrations, three if possible, for each test period.

4. General observations concerning behavior will be made. These include increase or lack of movement, erratic movement, loss of equilibrium (partial or complete), and any uncommon reaction to the test chemical.

5. Simple graphic interpolations of dose effect will be made in order to derive a 96-hour TLm (medium tolerance limit) and in addition Lichfield and Wilcoxon's probit analysis method will be employed to derive the LC, LC_{50}, and LC_{99} and their confidence limits for each 24-hour test period.

6. All tests will be conducted in one dilution water, a soft water and at one temperature.

This method gives the ED_{50}, slope of the curve and their confidence limits. It uses original data throughout and uses 0 and 100 percent effects. The method recognizes heterogeneity when present and gives corrected confidence limits in such cases and facilitates the comparison of two curves for parallelism and computation of relative potency with its confidence limits. The method is rapid and is used without logarithms. Logarithmic-probability paper is used to plot data in original units (i.e., percentages and arithmetic values) equivalent to the use of logarithms and probits. Nomographs are used to allow a simple arithmetic solution of a dose effect curve which is equivalent to the solution by use of logarithms and probits. This method is recommended by Pesticides Regulation Division Animal Biology Section U.S.D.A. and we have found it to be very effective.

Specific Bioassay Test Techniques (fish and snail)

1. The fish bioassay experimental technique will consist of a pump-fed system which meters calculated amounts of test sample and aerated dilution water separately into a head jar where they are mechanically mixed by magnetic stirrer. The mixed concentration of sample in dilution water then flows a a fixed rate into the bottom of a five-gallon wide mouth glass test container holding ten test fish. The used mixture of test sample in dilution water overflows the top of the test jar at the same rate that the new mixture enters the bottom of the test jar. The rate of flow is one gallon per hour

which past experience has shown is sufficient to maintain physiological dissolved oxygens and CO_2 levels. Twenty fish are exposed to each concentration in the test series, ten for each of two bioassay test systems, 0.5 to 1.0 grams fish per liter of test water. Test fish will be obtained from a hatchery, transported to the test site in water comparable in temperature and quality to that used in the hatchery and will be acclimated in the laboratory for at least two weeks at the test temperature before use in the bioassay tests. Test fish will receive no food for 36 hours prior to a test or during the test period to minimize waste production during the exposure period.

3. Snail bioassay experimental techniques will consist of the same system as outlined above for the fish bioassay except that the test containers will be 32 ounce glass jars with lids. Used test water will overflow through a screened hole in the lid so that no air space exists in the test jar which would allow the test snails to remove themselves from the test solutions. Test snails will be obtained from local waters. They will be acclimated in the laboratory in the same manner as the test fish.

Specific Bioassay Test Technique (Diatom)

The method used is ASTM D2037-64T "Tentative method of test for evaluating inhibitory toxicity of industrial waste waters". This refers to diatoms as part of the fish-food chain. Although it somewhat resembles the PAAP test for biostimulation, both test programs are considered necessary.

B. Detailed Acute Testing Procedures (account of an actual test)

1. Fish

The Test Organism - The bluegill sunfish, *Lepomis macrochirus* Raf., which has a wide distribution, was used for test purposes.

The fish used in the tests were between 4 and 6 cm in length measured from the anterior tip of the head to the end of the caudal fin, or tail. In no individual test did the length of the largest specimen exceed the length of the smallest by more than 50 percent. The fish were acclimated in the laboratory for a period of two weeks at the test temperature of 18°C. Test organisms received no food for 36 hours before a test or during the test period. Each fish was used for only one test; only healthy fish were used. Stock cultures which had more than 5 percent mortality during the period of acclimatization were discarded.

Apparatus - The continuous flow experimental technique consisted of a pump-fed system which metered calculated amounts of sample and dilution water separately into a head jar where they were mixed. The mixed concentration of sample in dilution water then flowed at a fixed rate into the bottom of a 15 gallon glass stainless steel framed aquarium in which were placed 20 test fish. The used dilution water overflowed the top of the aquarium at about the same rate that new dilution water entered the bottom of the aquarium. The rate of flow was one gallon per hour. This was allowed to proceed for 96 hours for each experimental concentration.

In all tests constant dilution waters were prepared from distilled water and A.C.S. grade chemicals. Each chemical was pipetted separately from a concentrated (200X) stock solution directly into distilled water in order to prevent the precipitation of chemicals. Carbon dioxide was bubbled through the dilution water to get all the chemicals into solution. The dilution water was then aerated until the saturation point of oxygen was reached and the CO_2 brought to the normal level. Dissolved oxygen was determined by the oxygen meter before the fish were introduced and every hour for six hours thereafter. At least four D.O. readings were made during each 24-hour test period.

Conditions of the Tests

Constant Temperature:	18°C
Dissolved Oxygen:	5 to 9 ppm
Dilution Waters:	A prepared water similar in chemical characteristics to a soft water referred to as modified CHU 14.

	gms/liter
KCl	0.02
Na_2SiO_3	0.02
$NaHCO_3$	0.04
$MgSO_4 \cdot 7H_2O$	0.04
$Ca(NO_3)_2 \cdot 4H_2O$	0.04
$CaCO_3$	0.01
K_2HPO_4	0.002
Ferric nitrate	0.0018

The dilution water was made up from distilled water to the quality indicated above.

Addition of Test Organisms

Twenty fish, 4 to 6 cm long, were added to the mixed solution after the dissolved oxygen had been raised to the required level.

Control

A control tank was maintained with each experiment. In each control tank 100 percent survival was required.

Calculation of the Biologically Safe Concentration

Application factors for calculation of Biologically Safe Concentrations are presently being discussed and several recommendations for these factors are available. Perhaps one of the most recent and authoritative recommendations comes from the Report of the Committe on Water Quality Criteria, FWPCA, U. S. Department of Interior, 1968. From the section on "Water Criteria for Fish and Other Aquatic Life" the proposal is made that "Concentrations of materials with non-cumulative toxic effects should not exceed 1/10 of the 96-hour TLm value at any time or place. The 24-hour average of the concentration should not exceed 1/20 of the TLm value."

The above recommendation is probably the most widely accepted application factor by state and federal agencies at this time.

2. Snail

The Test Organism - Amnicola limosa (Say.), a gilled snail, was chosen for test purposes. The snails used were adults averaging 3 mm in diameter. They were collected from the Brandywine Creek, East Branch, outside of West Chester, Pennsylvania.

The snails were acclimated in the laboratory for a period of four weeks to the dilution water. Test organisms received no food for 36 hours before a test or during a test period. Each snail was used for only one test and only healthy snails were used for test purposes.

Apparatus - Containers for snail tests were 1500 ml jars. Each jar was fitted with a plastic lid and the lids were perforated to allow for gas exchange. Calculated amounts of test samples and dilution water were pumped in two separate streams to a head jar where they were mixed and the mixture then flowed into the bottom of the test container at the rate of 100 mls. per hour. The used mixture overflowed the top of the container at the same rate. The test period was 96 hours. Dissolved oxygen was determined by the modified Winkler method before the snails were introduced. Two D.O. readings were made during each 24-hour test period.

Conditions of the Tests

Same as Fish Tests.

Addition of Test Organisms

Twenty adult snails were added to the mixed solution as soon as the dissolved oxygen had been raised to the required level.

Control

Same as with Fish.

Calculation of the Biologically Safe Concentration

Same as with Fish.

3. Diatom

The Test Organism - Navicula seminulum var. hustedii Patr., is a moderately sensitive fresh-water diatom common to many undisturbed streams.

The diatoms were cultured for several months prior to the test period in 500 ml Erlenmeyer flasks, containing soft water nutrient solutions.

These stock cultures were maintained at 18°C ± 1°C. Light, an important factor in the growth of diatoms, was provided by two 85 watt daylight fluorescent lamps located about six inches below a glass shelf, furnishing an illumination of approximately 250-350 foot candles. The cultures were placed on the shelf, and received 16 hours of this illumination. Cultures were agitated constantly to insure even distribution of the diatoms throughout the flask.

Apparatus for Tests

The batch tests were conducted in sterile 125 ml Erlenmeyer flasks. In each of the specific concentrations of sample in dilution water there was a total of 50 mls of liquid. This provided a relatively large surface-to-volume ratio, and thus allowed full exchange of gases in the air.

Conditions of Tests

Temperature:	18°C + 1°C.
Light:	250-350 foot candles and as for stock cultures above.
Dilution water:	Same as Fish with the addition of soil extract and micrometabolic solution.

Agitation

The batch tests were placed on a shaker during the 7-day test period to insure an even distribution of the diatoms.

Addition of the Test Organisms

The inoculum was made uniform with the use of a Waring Blender. One milliliter of the inoculum is pipetted into each test flask. After seven days each flask is scraped clean and the contents blended. Then cell counts are made of diatoms. These counts are compared to the control to determine the reduction in growth.

Calculation of the Median Tolerance Limit

In calculating the effect of any sample, the concentration which produced a 50 percent reduction in growth is considered as significant for diatoms.

In most cases no concentration in these tests produces exactly a 50 percent reduction in growth, and it is usually necessary to determine this value by graphic interpolation of the test results. The 50 percent reduction in growth concentration corresponds approximately to the median tolerance limit (TLm) for fish.

IV. CHEMICAL, PHYSICAL AND TOXICOLOGICAL PROPERTIES

A. Chemical and Physical Properties

Characterization and standardization of detergent ingredients is particularly important because small differences in purity or composition often make a big difference in performance. Chemical characterization includes assurance and reproducibility of molecular structure, stability against hydrolytic or oxidative decomposition or other types of chemical change under storage or use conditions, and quantitative knowledge of minor contaminants that may have a significant effect on overall behavior. On this basis we propose to check the various ingredients used in the detergent formulations in the following manner. Manufacturers and suppliers' specifications with regard to chemical structure will be used except when they are inadequate (incomplete) or where we have reason to suspect that they are inaccurate. In such cases, using ASTM methods of test wherever available, the following characterization tests will be applied: Builders will be checked for sequestering power by the soap or oxalate titration methods given for example in Chabarek and Martell "Organic Sequestering Agents," or by other appropriate methods. Surfactants will be checked for active ingredient content and neutral oil (unsulfonated matter) content. Polymeric materials will be checked by viscosity for average molecular weight (paying attention to polyelectrolyte effects in the measurements) and by chemical analysis for degree of substitution (where indicated). If indicated, gel permeation chromatography will also be used. All major ingredients will be checked for trace elements, using atomic absorption spectroscopy and/or emission spectral analysis. This is considered important because trace elements can have a significant effect on the biological effects of the product, particularly the biostimulation. Final formulations will require checking for stability, since many detergent ingredients tend to suffer hydrolytic degradation during drying or other stages of preparation. Tests for degree of degradation are routine but they vary with the type of surfactant or builder involved.

Physical properties of importance include solubility and rate of solution at various temperatures, bulk density, dustiness, and physical homogeneity. Physiological effects of the final formulations are obviously of paramount importance. These include toxicity (by ingestion as measured by LD-50 values on test animals) skin irritation and sensitization and eye irritation. They will be determined by methods outlined below.

B. Toxicological Properties

Background - A toxicity testing program to evaluate the safety of detergents must be designed to include the intended use of the product. Obviously, testing of a detergent composition intended for general use, such as laundering and dishwashing, has to be more inclusive than of one intended just for machine laundering. A general purpose household detergent product can be evaluated by methods similar to those described by Snyder et.al. (1964) and Opdyke et.al. (1964). These include: acute oral toxicity and emetic dosing to evaluate accidental ingestion hazards; chronic oral toxicity to evaluate ingestion from residues on dishes and cooking utensils; subacute percutaneous toxicity to evaluate continuous exposure to skin from residues on hands and clothing; human patch test studies to evaluate the irritancy or sensitization potential of the detergent; opthalmic irritancy in rabbit eyes to determine the hazard to eyes from accidental exposure; and tumorigenic activity as measured by repeated topical and subcutaneous applications to mice. Because we propose only preliminary testing, in preparation of a consumer test, our proposal below is not so all inclusive.

Test Methods - The studies proposed here are sufficient to evaluate, in a preliminary way, the medical safety of a heavy-duty household detergent composition intended for machine laundering. The animal tests listed below by themselves are intended to screen the medical suitability of an ingredient for including in household product. The combination of these animal tests and the human studies described below are designed to evaluate the detergent to a degree sufficient for a Consumer Test where human exposure is limited in numbers (say up to 500 people) and in duration (say up to one month of normal use). More complete testing would be necessary before the formulation should be sold to larger numbers of people.

Acute Oral Toxicity - Healthy, young albino rats ranging in body weight from 125 to 200 grams will be used as test animals. All animals will be kept under observation at least seven days prior to experimental use, during which period they will be checked for general physical health and suitability as test animals. The animals will be housed in stock cages and permitted a standard laboratory rat diet plus water *ad libitum* until 16 hours immediately prior to oral intubation.

Initial screening will be conducted in order to determine the general level of toxicity and then selected dose groups of four rats each (two male and two female) will be intubated with previously calculated doses of the test material. All doses will be administered directly into the stomachs of the rats using a hypodermic syringe equipped with a ball-pointed intubating needle.

Following oral administration of the test material, the rats will be housed individually in observation cages (10" x 8" x 8") and observed for the succeeding 14 days. Initial and final body weights as well as all mortalities and/or reactions displayed will be recorded. Arrangements will be made to autopsy any animal which might succomb during the study as well as all surviving animals at the end of 14 days.

At the end of the observation period, all data will be collected and arrangements will be made to calculate, if possible, the acute oral median lethal dose (LD_{50}) of the test material using the techniques of Weil (1952), Thompson (1947), and Thompson and Weil (1952).

Acute Dermal Toxicity - Young adult, New Zealand strain albino rabbits ranging in body weight from 2.3 to 3.0 kilograms will be employed as test animals. All rabbits will be kept under observation in the laboratory for seven days prior to testing during which time the animals will be examined with respect to their general health and suitability as test animals. The rabbits will be housed individually in hanging rabbit cages and maintained on a standard laboratory rabbit ration. Food and water will be permitted *ad libitum.*

Twenty-four hours prior to the dermal applications, the backs of the rabbits will be shaved free of hair with electric clippers. The shaved area on each animal will constitute about ten percent of the total body surface area. The animals will then be returned to their cages to await testing on the following day. The 24-hour waiting period will allow recovery of the stratum corneum from the disturbance which accompanies the close-clipping procedure and also will permit healing of any microscopic abrasions possibly produced during the process.

On the testing day, the rabbits will receive skin applications of the test material at several selected dose levels. Groups for each dose level will consist of four rabbits (two male and two female). After each application, the exposure site will be covered by wrapping the trunk of the animal with an impervious plastic sheeting which will be securely taped in place. This plastic wrap will insure intimate contact of epidermis and test material. To further prevent oral ingestion of the test material, each animal will be fitted with a lightweight flexible plastic collar which will be worn throughout the observation period.

The test material will remain in contact with the skin for 24 hours. Any reaction displayed by the animals will be observed and recorded, during the contact period, after which the plastic sheeting will be taken off each test rabbit and all residual test material removed. The exposure sites will be examined for local skin reactions and the animals returned to their cages. Observations for mortality, local skin reactions, and behavioral abnormalities will be continued for a total of 14 days following the skin applications. Initial and final body weights will also be recorded. Arrangements will be made to autopsy any animals which might succumb during the study as well as all surviving animals at the end of the observation period.

At the end of the observation period, all data will be collected and arrangements made to calculate, if possible, the acute dermal median lethal dose (LD_{50}) of the test material using the techniques of Weil (1952), Thompson (1947), and Thompson and Weil (1952).

Opthalmic Irritation - Five young adult albino rabbits of the New Zealand strain will be used to evaluate the eye irritating properties of the test material.

The test method employed will be patterned after that of Draize et al. (1944). Exactly 0.1 ml or 0.1 g of a test material will be instilled into the conjunctival sac of the right eye of each test rabbit. The left eye of each animal will serve as a scoring control.

One, 24, 48, 72, 96 hours, and 7 days following the initial instillations, the cornea, iris, and palpebral conjunctiva will be examined individually and graded for irritation and injury according to a standard scoring system. The maximum possible score at any one examination and scoring period is 110 points which indicates maximal irritation and damage to all three ocular tissues. Zero score indicates no irritation whatever. The scoring system is presented in the following Table.

Eye Irritation Test - Albino Rabbits

Scale of Weighted Scores for Grading the Severity of Ocular Lesions

I. Cornea

A. Opacity - Degree of Density (area which is most dense is taken for reading)	
Scattered or diffuse area - details of iris clearly visible	1
Easily discernible translucent areas, details of iris slightly obscured	2
Opalescent areas, no details of iris visible, size of pupil barely discernible	3
Opaque, iris invisible	4

B. Area of Cornea Involved	
One quarter (or less) but not zero	1
Greater than one quarter but less than one-half	2
Greater than one-half but less than three quarters	3
Greater than three quarters, up to whole area	4

Score equals A x B x 5   Total maximum = 80

II. Iris

A. Values	
Folds above normal, congestion, swelling, circumcorneal injection (any or all of these or combination of any thereof), iris still reacting to light (sluggish reaction is positive)	1
No reaction to light, hemorrhage, gross destruction (any or all of these)	2

Score equals A x 5   Total maximum = 10

III. Conjunctiva

A. Redness (refers to palpebral conjunctiva only)	
Vessels definitely injected above normal	1
More diffuse, deeper crimson red, individual vessels not easily discernible	2
Diffuse beefy red	3

Eye Irritation Test - Albino Rabbits (Continued)

III. Conjunctiva

B. Chemosis

Any swelling above normal (includes nictitating membrane)	1
Obvious swelling with partial eversion of the lids	2
Swelling with lids about half closed	3
Swelling with lids about half closed to completely closed	4

C. Discharge

Any amount different from normal (does not include small amount observed in inner canthus of normal animals)	1
Discharge with moistening of the lids and hairs just adjacent to the lids	2
Discharge with moistening of the lids and hairs and considerable area around the eye	3

Score (A + B + C) x 2 Total maximum = 20

Note: The maximum total score is the sum of all scores obtained for the cornea, iris and conjunctiva.

Rabbit Primary Skin Irritation - Four young adult albino rabbits of the New Zealand strain will be used in the evaluation of primary skin irritating properties of the test material. The test procedure employed will be modeled after that of Draize et.al. (1944).

Prior to the application of the test material, the hair will be clipped from the backs and flanks of each rabbit. Two test sites located at the midline of the back approximately ten centimeters apart will then be selected. One of the two sites will be abraded by making four epidermal incisions, two perpendicular to the other two, while the other skin site will remain intact.

Exactly 0.5 ml or 0.5 g of the test material will be applied to the prepared exposure sites on each rabbit and immediately occluded with square gauze patches, two inches on a side. These will be affixed directly over the skin test sites and secured in place with masking tape. Following the patch applications, the entire trunk of each test animal will then be wrapped in an impervious plastic sheeting. This will help hold the patches in position and retard evaporation during the 24-hour exposure period.

At the end of 24 hours, the plastic wrappings and patches will be removed. The intact and abraded skin sites will then be individually examined and scored separately for both erythema and edema on a graded scale of 0 to 4. After 72 hours had elapsed, the sites will be re-examined and rescored.

In evaluating the average irritation present, the mean scores for erythema and edema of the intact skin sites at the 24- and 72-hour reading intervals will be added. Similarly the mean scores for erythema and edema of the abraded skin sites at the 24- and 72-hour reading intervals will be added. These two values will then be totaled and divided by four to obtain the mean primary irritation score. The scoring criteria for erythema and edema are shown in the following Table.

Table

SCORING CRITERIA FOR SKIN REACTIONS

Reaction	Description	Score
Erythema	Barely perceptible (Edges of area not defined)	1
	Pale red in color and area definable	2
	Definite red in color and area well defined	3
	Beet or crimson red in color and/or injury in depth (necrosis, escharosis)	4
Edema	Barely perceptible (Edges of area not defined)	1
	Area definable but not raised more than 1 mm	2
	Area well defined and raised approximately 1 mm	3
	Area raised more than 1 mm	4
	Maximum Primary Irritation Score =	8

Human Primary Irritation and Sensitization - Semi-occlusive Patch Test Procedure, 9-Day - 24 hours. (Eight repeated insults plus one challenge patch.)

This is a combined over-night primary irritancy and/or sensitization test. Patches are applied Monday, Tuesday, Wednesday, and Thursday to the same skin sites and allowed to remain on for 24 hours.

Readings are made shortly after the patches are removed on Tuesday, Wednesday, Thursday and Friday. Following two weeks of patching and two rest weeks, a challenge patch is applied and readings taken at 24, 48 and if necessary at 72 hours.

A panel of 50 subjects are employed on this test. Four materials including controls can be run on this test. Two types of patches are used on this test: 1) Closed elastopatch (Duke) 1-1/2" x 2" with 3/4" x 1" special pad and 2) Semi-open elastoplast (Duke) protective covering for patch test 1" x 2" with 1" x 1" Webril (R) pad.

The material is applied to the patch which is then placed on the surface of the upper arm. A marker (Gentian Violet) is used to indicate the patch position on the arm. Readings are taken approximately 24 hours after each patch application. Following each reading, a new patch is applied to the same unless the severity of the reaction prohibits repatching. For the challenge application, patches are applied to adjacent sites on the arm. A second challenge is made if there is a reaction to the first.

In most, if not all instances, the test product will be a solid material. For the tests described above, it will be applied to the animal as a dilute, aqueous solution, approximately 5 percent wt/vol. For human testing, the products will be tested as 1 percent wt/vol. aqueous solution.

References - Preliminary Mammalian Toxicity Testing

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Provisional Test For Screening Potentially Corrosive Products[1]

Method

Four healthy, adult, albino rabbits of either sex (weight range 2-3 kg.) will be used to test each material. The animals will be fasted for 48 hours prior to testing with water available ad libitum. Each animal will be anesthetized[2] with sodium pentobarbital, and the oral cavity will be examined with the aid of a binocular loupe (magnification 2-3X) and examining lamp. After recovery from anesthesia, the animals will be placed in a restrainer, and the mouth forced open with a plastic bit containing a 1/2" to 3/4" hole in the center. The tongue will be drawn forward through the hole with a pair of long forceps. A curved spatula or syringe will be used to administer the dose (300-500 mg. of dry material, or 1 ml. of liquid) on the posterior aspect of the tongue. The tongue will be released immediately allowing the animal to complete the swallowing reflex. The animal will be returned to its' cage with access to water, but no food. At 24 hours, two of the test group will be sacrificed by overdose of anesthetic (pentobarbital IV). The surviving animals will be given food, and sacrificed at 96 hours. The tongue, adjacent pharyngeal structure, esophagus, and stomach will be removed, examined grossly, and photographed (color). After thorough evaluation, these tissues will be preserved in neutral buffered formalin for subsequent microscopic evaluation as necessary.

Evaluation for corrosivity will be based on visible effects on the oral cavity, pharyngeal structure, esophagus, and stomach. Each test material will be arbitrarily classified as follows:

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1. This is not an official test procedure.
2. If the animal's mouth can be examined easily without any discomfor or anesthetic, the problems of anesthesia can be eliminated.

a. Negative - No visible irritation or injury when examined at 24 or 96 hours. Histopathology may not be necessary as determined by gross examination.

b. Irritant - Patchy areas of beefy redness with or without edema present at 24 hours, but not at 96 hours. Histological examination of tissue from the animals sacrificed at 96 hours should be normal in appearance.

c. Corrosive - Necrotic lesions (i.e., esophageal perforation, stricture, etc.) apparent at 24 or 96 hours will be confirmed by microscopic examination.

Since the test is primarily concerned with corrosive action, it will be considered positive if any of the test animals at 24 or 96 hours show signs of necrotic lesions in the mouth, pharynx, esophagus, or stomach. The extent of injury will be confirmed by histological examination. Microscopic examination of tissue sections will not be performed in the absence of visible irritation. Close-up photographs will be considered as sufficient documentation. When gross lesions are present or for borderline cases, histopatholgy will be performed in addition to photographs. Color photography will be utilized as often as warranted to provide a vivid documentation of gross effects.

APPENDIX B

LAUNDERING TEST METHODS DEVELOPMENT

Detergent technologists and scientists have never been able to agree upon any single simple laboratory test for measuring the soil removing power (laundering effectiveness or washing power) of a detergent. The basic experiment is simple and straightforward in concept. A set of fabric swatches is soiled in some controlled manner to a uniform degree of dirtiness. Some of the swatches are then washed in detergent A and others in detergent B, keeping the detergent concentrations, temperatures, and other parameters of detergency constant. The washed swatches are then measured optically to determine which have lost more soil. Disagreement arises over details of the test, especially over the type of soil that is used and the method by which it is applied to the swatches. Each of the important laboratories of the detergent industry has its own screening protocols and its own procedures for obtaining detergency data that they consider accurate (i.e. representative of results that will be obtained in actual home laundry practice). The details of these methods are not publicly divulged. The one method for evaluating washing power that is agreed upon is an actual miniature field trial under household conditions, known as the bundle test. This test has been reasonably well standardized, at least in general format, and is described as ASTM Standard D2960-71T. The bundle test, however, is far too lengthy and cumbersome to be used as a test method in research. It was therefore necessary to adopt (or develop if necessary) a set of screening procedures that would at least be respected by all major segments of the industry even though it might not coincide with their own favorites. Throughout the program, therefore, special attention was paid to refinement and variation of the test methods even though this required a significant amount of laboratory work. The lengthier and more extensive testing programs were reserved for the more promising candidate detergents, but modifications of the simpler tests were adopted as soon as they were proved to be valid and useful. The various procedures, their modifications, and the experimental work connected with their interpretation and validation are as follows:

A. The primary screening test for laundering effectiveness used in this program was a soil accumulation test, following the general model given in articles by Schwartz and Berch, Soap and Chemical Specialties, 39, 78, (May, 1963); Spangler, Cross and Schaafsma, J. Am. Oil Chemists Soc. 42, 723 (1965); and Schwartz and Rader, J. Am. Oil Chemists Soc. 42, 800 (1965). In this type of test one or more unknown detergents are compared against a standard detergent under identical conditions of soiling and washing. To illustrate the procedure for one unknown detergent: two identical sets of clean test swatches are soiled simultaneously in a single large pool of soil. The sets are then separated and washed separately, one set in the standard detergent "S" and the other in the unknown detergent "X". After washing and drying they are resoiled and again separated and washed, each set going to its own detergent. After several cycles of soiling and washing the sets are again measured for reflectance. Even when two detergents are very close in cleaning power a significant difference in the set averages can usually be found after about 5 cycles. Included with each set are some swatches that go through the washing and drying steps but not through the soiling step. These swatches accumulate soil by redeposition from the wash bath, and the decrease in their reflectance is a measure of the antiredeposition effect of the detergent. A wide variety of soils can be used, but some type of "natural" soil is generally preferred.

The Tergotometer was used as the washing device, run at either 100 or 125 cycles/minute. Three types of white fabric were used in the early stages of the program: a permanent press 65 polyester-35 cotton blend; a bleached but unfinished cotton print cloth; and an unfinished 100% polyester. The three types of fabric were all washed simultaneously in one bath, the load consisting of 3 soiled swatches and 2 redeposition swatches of each fabric, a total of 15 swatches in each one liter bath. The swatches measured about 4.5 x 6 inches and averaged about 2 grams each in weight.

Both the water hardness and the temperature can be varied as desired, but must be controlled and specified in the report. Our primary test was made with 200 ppm water (4:1 Ca to Mg ratio) at 120°F. The washing time was 10 minutes. To ensure that the detergent was performing at full effectiveness, i.e., that we were in the plateau region of the soil removal v. concentration curve, the formulations were used at 0.3% concentration.

Two types of soil were used: a "dry" soil and an "oily" soil, both of which were based on the dirt swept from rugs by vacuum cleaning. The dirt was procured in large lots (20-50 pounds or more) from a commercial rug cleaning establishment. It was processed by slurrying in tap water and then filtering through cheesecloth and muslin to remove lint and large particles. Quantity of water was adjusted so that the final filtered slurry contained about 2% solids. The soil was also checked to ensure that no soluble staining materials were present. Batches of soil containing staining materials were rejected. The 2% solids slurry thus prepared constituted the "dry" soiling bath. A small amount of preservative was added. The "oily" soil was prepared by adding sufficient artificial sebum (prepared according to Spangler, Cross and Schaafsma, loc. cit.) to provide a sebum-to-solid soil ratio of about 2 to 1. The water content was adjusted so that the final slurry contained about 1.5% sebum-plus solid soil.

As standard detergents in these tests we used Formulation #124, furnished by the American Association of Textile Chemists and Colorists. This material is described as follows:

Standard AATCC Detergent

Lot 1-1 & Lot 2-1

Nominal Composition	%
Linear alkylate sulfonate - sodium salt (LAS)	14.0
Alcohol ethoxylate	2.3
Soap - high molecular weight	2.5
Sodium Tripolyphosphate	48.0
Sodium silicate ($SiO_2/Na_2O = 2.0$)	9.7
Sodium sulfate	15.4
CMC	.25
Moisture & Miscellaneous	7.85
	100.00

In Standard Detergent with optical brightener (Lot 1-1 only) the miscellaneous includes approximately .25% of a mixed brightener system including balanced proportions of bis [triazinyl] stilbenedisulfonate, and triazolystilbenesulfonate with a potential specialty brightener.

In the earlier phases of the program Lot 1-1 was used, and is referred to in the text simply as AATCC or AATCC #124 detergent. At a later stage Lot 2-1 was used. This is referred to as AATCCWOB.
Lot 1-1, which contains brightener, was the only standard reference detergent available at the start of the program, and it was considered desirable to use in addition a reference detergent without brightener. A supply of such a detergent was obtained from The Association of Home Appliance Manufacturers. This is referred to as the

AHAM detergent, and has the following composition:

Tallow Soap	2%
Dodecylbenzene Sodium Sulfonate	14%
Nonionic Pluronic Type	2%
Sodium Tripolyphosphate	50%
Trisodium Silicate (2:1)	6%
NaCMC	0.5%
Sodium Sulfate	17%
Water	8.3%
Miscellaneous	0.2%

B. The above procedure, using "dry" and "oily" (or "sebum") vacuum cleaner soil, was modified during the course of the program in two respects, both of which simplified the testing and neither of which changed the results to any significant extent. The first modification consisted in using only three wash-soil cycles instead of four. At the soil concentrations used it was found that three cycles were sufficient. The second modification was a change in the method of preparing oily soil swatches. Instead of combining the aqueous sebum emulsion with the suspension of solid vacuum cleaner particulates and soiling in a single step, a two step process was adopted. In this process the first step was to prepare dry soiled swatches in the usual manner. These were then wet to saturation with a perchloroethylene solution of the artificial sebum ingredients, and were then air dried. This process afforded much better control and produced more uniform and reproducible swatches than the one step procedure.

C. A third wash testing procedure adopted and used during the course of the program was essentially that described by Spangler, Cross and Schaafsma (J. Am. Oil Chemist's Soc., 42, 723 (1965). This is a multicycle soil-accumulation test of the same type as the tests described in section A above. The soiling mixture is an aqueous emulsion containing the artificial sebum ingredients and particulate solids obtained from air conditioner filters. To prepare the solids portion of this mixture used air conditioner filters were washed with isopropanol. This solvent stripped the filter fibers clean very rapidly and easily. The washings were filtered on a Buchner funnel, and the recovered solids were dried and ground. They were a very dark gray in color, very finely divided (requiring little or no sieving to remove lumps) and easily dispersed in the artificial sebum emulsion. This soil is referred to in the body of this report as "Spangler soil" and was always used in the three cycle soil accumulation procedure.

D. Primary screening test of washing power are usually made, as outlined above, at a single detergent concentration. For a more thorough evaluation it is necessary to measure the washing power at a series of concentrations. This can be done using a multicycle test procedure, as were some of the washing power evaluations in this program, but it is inordinately time consuming. Single cycle tests are usually considered adequate for detergency v. concentration studies. Soil cloth suitable for single cycle testing can be purchased commercially. In our experience, however, few if any of the man-made fiber soil cloths or the permanent press finished soil cloths are sufficiently realistic or reliable. One commercial cotton soil cloth, "Empa" from Testfabrics, Inc., New York, was used in some of the detergency v. concentration studies. For most studies of this type on cotton, and for all such studies on other fabrics, we prepared our own soil cloth as follows:

The soiling mixture was similar to the Spangler soil except that the air conditioner dirt was replaced by a mixture of particulates consisting of 86% kaolin (Bandy Black #1 clay), 8% carbon (Germantown Lampblack), 4% Mapico black iron oxide and 2% Mapico yellow iron oxide. The aqueous soil suspension was applied by padding. By setting the pad rolls at a pressure (about 50 psi) such that the wet pick-up was about 100%, and by running the fabric through the pad forward and reverse twice, large single pieces of fabric were soiled uniformly and reproducibly. These could be cut into test-size swatches which matched one another so closely in reflectance that they did not have to be sorted nor read individually before use. This is referred to as "Colgate soil."

E. The instrument used for measuring reflectance was a Gardner XL-10 Color Difference Meter. The filters are such that it can read green (G) amber (A) blue (B) and blue free of u.v. (Bx). The three readings made routinely were G, A and Bx. The G reading by itself is generally considered a good basis for comparing the appearance of cleanness presented by a fabric swatch, and the delta G values were used for comparisons in most of the earlier work. From the three primary reflectance readings, however, two additional reflectance parameters can be calculated: "whiteness" (W) = 4Bx - 3G; and "yellowness" $= \frac{A-Bx}{G}$. This was done routinely in the computer program. It was found after bundle testing had been started, and visual judgments were being compared with instrumental readings, that the W value was usually a better index than the G value of the visual ratings. The W value was therefore adopted as the main basis for comparison. The Y value was important in cases where either the detergent or the fabric finish changed the tint of the test swatches. Such cases are noted in the text. Table headings in all cases indicate which reflectance parameter is being considered.

F. Bundle tests were made on seven formulations, the general procedure of ASTM, D2960-71T being followed in all cases. Rockville, Maryland, tap water, averaging 110 ppm, was used. In the first three tests the detergent formulation was used at 0.2% concentration and instrumental readings were made only on pillowslips. The formulations were as follows: (1) #64-1, also identified as "D", based on citrate builder and ether carboxylate 60-486 surfactant. (2) #64-2, also identified as "M", based on citrate builder and sulfozwitterionic surfactant 54-431. (3) Composition B-S based on SHIM builder and alpha olefin sulfonate surfactant 22-155. Two subsequent runs identified as 242 and 242a were made at 0.15% concentration, with pillowslips read instrumentally. At this low concentration even the control detergent AATCCWOB did not get the laundry satisfactorily clean. The last three tests identified as 269, 270 and 271, were therefore made at 0.3% concentration. In these latter tests all laundered items were read instrumentally. The instrumental readings checked the panel judgments without exception.

G. An essential part of the methods development program was to compare the three multicycle and two single cycle wash tests outlined above with one another and with the bundle test. This task was carried out, and was written up and presented in the form of a paper at the CID's International Congress on Surface Activity, Zurich, September 1972. Title and authors are: "Soil Accumulation versus Bundle Testing of Detergency," H. Alter, A. Eleanor Davis and A. M. Schwartz. It is scheduled for publication in the Congress Proceedings. The following is an abridgement of the paper.

EXPERIMENTAL

Five test procedures were used. Procedure #1 was single cycle using Empa cotton. Procedure #2 was single cycle using Colgate soil.

Procedure #3 was multicycle Spangler soil. Procedure #4 was multicycle "dry" vacuum cleaner soil, and procedure #5 was multicycle "sebum" vacuum cleaner soil, as described above. All except procedure #1 were carried out on both cotton and durapress (DP) 50 cotton: 50 polyester fabric. The prepared swatches were read on the reflectometer before and after washing. Alcohol extractable material was determined on washed swatches and on representative swatches before washing.

The Tergotometer load consisted of 10 swatches, 6 soiled and 4 unsoiled (redeposition) swatches. In all but procedure 1 the load was split evenly between cotton and durapress swatches. The volume of detergent solution was 700 ml, and the pH of the detergent solution was checked before and after washing. Agitator speed was 125 cycles/min. Wash temperature was 120°F and wash time 10 minutes. The swatches were given two one minute rinses at 105°F. After rinsing the swatches were squeezed out, spread flat on cheesecloth and oven dried at 120°F for 15-20 minutes.

Reflectance was measured at 4 areas (2 front and 2 back) on each swatch. The swatches were layered and folded for measurement to provide 5 thicknesses of backing for soiled swatches and 3 thicknesses for redeposition swatches. Readings were made with green, amber and blue X filters. The data were automatically punched into computer tape for processing.

Alcohol extractable matter was measured in the standard manner via Soxhlet extraction with ethanol.

Three detergents were used in the bundle tests. The primary standard-of-comparison detergent was the high phosphate formulation furnished as a reference by the Association of Home Appliance Manufacturers (Identified as AHAM detergent). This material contained no fluorescent whitening agent. The other two detergents were experimental nonphosphate materials. Both contained 20 percent high ratio silicate and 30 percent citrate as the builder. "Detergent D" contained 20 percent fatty alkyl ether carboxylate as the surfactant. "Detergent M" contained 20 percent of sulfo-zwitterionic surfactant. Both detergents contained 1 percent sodium carboxymethylcellulose, 29 percent sodium sulfate, and no fluorescent whitening agent.

The above three detergents were also used in the Tergotometer tests, together with another high phosphate type furnished by the American Association of Textile Chemists and Colorists identified as AATCC #124 and herein abbreviated "AATCC". Detergent AATCC contained brightener (fluorescent whitening agent) and was therefore not used in the bundle tests where the ratings are subjective. It was used in all the other tests where the ratings were instrumental, and the effect of brightener could be eliminated by using the green and/or Bx filter in the reflectometer.

The bundle tests were run at 0.2 percent detergent concentration in tap water (approx. 110 ppm hardness) at 50°C. In all other respects the conditions of ASTM D 2960-71T were followed. The Tergotometer tests were run at 0.1 percent, 0.2 percent and 0.3 percent concentration; in 200 ppm hard water (4 Ca to 1 Mg) as well as in tap water. All tests were run at the same temperature, time of wash cycle, and agitator speed.

RESULTS AND DISCUSSION

Bundle Tests

The bundle tests (0.2 percent concentration in tap water) were carried out to six cycles. The panel rated detergent D substantially equal to AHAM on both cotton and durapress items. It rated detergent

M clearly inferior to AHAM on both fabrics. Analysis of the data for detergent D with regard to fabric type showed that the panel chose AHAM somewhat more frequently than D on cotton items, and vice versa on durapress items.

Instrumental readings were made on pillowcases of both fabrics. The data, as shown in Table BG1, supports the subjective evaluations. D and AHAM are essentially equal in yellowness on both fabrics and in whiteness on durapress. D is very slightly inferior to AHAM in whiteness on cotton. M is significantly inferior to AHAM in whiteness on both fabrics and slightly inferior in yellowness on cotton.

There are many ways in which the reflectance data might be combined to give a single number purporting to correlate with the panel's subjective rating. No such combination, however, would be entirely free of arbitrary factors. It appears that graying was considerably more important than yellowing in this bundle test, but is entirely possible that with strongly yellow soils the yellowness rating would become more important and could dominate in correlating with the panel judgment.

It is noteworthy that the bundle test gives no indication of the amount of invisible soil, solid or oily, remaining in the fabrics after washing. The Tergotometer tests as performed in this study provide a direct measure of oily soil removal, via alcohol extraction. No measurement was made of residual invisible, alcohol-insoluble soil.

Tergotometer Tests Relatable to Bundle Tests

Tests using procedures 1 and 2 were carried out on cotton and on durapress at 0.2% concentration in tap water using the same three detergents used in the bundle test. The results of these tests are therefore most directly comparable with the bundle test results. Procedures 3, 4, and 5 were carried out on both fabrics with the same three detergents at 0.3% concentration in tap water, and are therefore comparable except for the difference in concentration. This difference can be considered minor since in tap water the detergency plateau of these detergents appears to be reached at a concentration less than 0.2%. Tergotometer tests at other concentrations and water hardnesses can be related only indirectly to the bundle tests.

Table BG2 presents the data for detergent D on cotton at 0.2% in tap water obtained by procedures 1 and 2. Columns 2, 3, and 4 show the delta G, delta whiteness and delta yellowness values (in reflectance units) relative to AHAM detergent. These values are computed as reflectance of AHAM washed sample minus reflectance of detergent D washed sample. Thus, a positive value means that AHAM was brighter, and a negative value that D was brighter. It is evident that the differences in yellowness are negligible and that the differences in delta G and delta whiteness parallel each other reasonably well. In view of the low yellowness values, ratings can safely be based on the whiteness ratings. On this basis procedure 1 rates AHAM best, followed in order by AATCC, M and D. The first three detergents are quite close to one another and D would be considered slightly but significantly poorer than AATCC or AHAM.

Columns 5 and 6 of Table BG2 give the actual percentage of alcohol extractable material in the D washed swatches before the first machine washing and after the last washing. Column 7 shows the comparison between AHAM washed samples and D washed samples. The number in column 7 is obtained by subtracting the column 6 value for D from the Column 6 value for AHAM (not shown in the Table), i.e.

Column 7 = Column 6 AHAM - Column 6 D

Thus, a negative value in column 7 indicates that the oily soil content of D washed material was higher than that of AHAM washed material, i.e. AHAM was the more effective in removing oily soil. The oily soil is a relatively low 1.19%, and none of the detergents was outstandingly effective in removing it. Although the data indicate AATCC most effective, followed in order by AHAM, D and M, the differences are small.

Procedure 2 rates the detergents with regard to whiteness in the order M best, D, AATCC and AHAM tied for poorest. With regard to oily soil removal there is substantially no difference between any of the four detergents. It is noteworthy that in procedure 2 the unwashed swatches have a relatively high content of alcohol extractables, a goodly portion of which remains after washing. Table BG2A gives the reflectance comparison of the redeposition swatches. It is evident that the differences are small as compared with the differences in reflectance of the soiled swatches.

Tables BG3 and BG3A give the numerical reflectance data for procedure 2 on durapress fabric. The differences are of the same order as those obtained on cotton. Tables BG4 and BG4A give the data for procedures 3, 4 and 5 on cotton at .3% in tap water; Tables BG5 and BG5A give similar data on durapress fabric.

A comparison of bundle test results with results of testing by the five different washing procedures leads to the following conclusions: 1. The whiteness reading, rather than the yellowness or individual filtered readings, is the most realistic single basis for relating to subjective judgment of appearance. 2. Soiled swatches are better than redeposition swatches as a basis for judgment. 3. Differences in whiteness values less than about 1.5 are not significant and do not correspond to a difference discernable by the panel judges.

This finding is supported by our previous experience. 4. With regard to alcohol extractable material, we have no basis for setting any numerical limit of significance on the delta values. We can rank the detergents as to their effect in removing oily soil, but whether or not these rankings have practical meaning is still an unanswered question.

Table BG6 shows the ranking of the various detergents on the basis of whiteness. The vertical bracket lines indicate a numerical difference between the bracketed items of less than 1.5 whiteness units. It is evident that procedures 1 and 2 are not sufficiently discriminating; although both procedures, when they do discriminate, do put AHAM ahead of M and D. In the one test where M and D are significantly different however (procedure 2, 0.3%, DP) they rank in opposite order to the bundle test. Procedures 4 and 5 definitely favor the non-phosphate detergents over the phosphate, a result opposite to that of the bundle test. Procedure 3 appears to match the bundle test results more closely than any of the other procedures. This may indicate that the air conditioner soil of procedure 3 is a better simulant than procedure 4-5 vacuum cleaner soil, at least for the soil in these particular bundle tests.

Tergotometer Test not Directly Related to Bundle Tests

Table BG8 comparing procedures 3, 4 and 5 in hard water at 0.3% detergent concentration, also indicates procedure 3 to be a better match than 4 or 5 for these bundle tests, although the conditions are not comparable. Table BG8 indicates that results in hard water tend to be much the same as in softer water, at least within the tested range. This is borne out by Table BG9 which shows the comparison of detergents M and D at increasing concentrations in hard water. The M and D ratings here can be compared with those of Table BG6.

Since a single cycle procedure is less arduous than a multi-cycle, and therefore would be desirable, an extended study of procedures 1 and 2 was made, with results shown in Table BG7. It is evident that procedure 1 is quite consistent, and sensitive neither to concentration nor water hardness. In rating M above D, however, it does not match the bundle test. This is probably due to the fact that the carbon black soil of procedure 1 is not a good simulant for the visible soil in the laundry bundles. Procedure 2 appears to be quite sensitive to both concentration and water hardness. Procedures 1 and 4 use low-oil soils, and procedures 2, 3 and 5 use high-oil soils. Tables BG2-BG5, together with extensive data on these systems not herein presented, indicate that an unsatisfactory amount of oil remains in the washed swatches when the high-oil soils are used, regardless of what detergent is used. Furthermore, the presence of excessive oil in the soil does not appear to contribute to consistency of results (as regards variations in hardness and concentration) nor to realism in matching the bundle test.

Redeposition data were obtained for all the tests tabulated. They generally bear out the data of Tables BG2A-BG5A, indicating that a high carboxymethylcellylose content improves the redeposition on cotton, and that redeposition is a much less sensitive index of performance than soil removal.

Conclusions

None of the procedures and soil mixtures used in this study has fully simulated the bundle test, although procedure 3 using air conditioner dirt as the colored soil ingredient is a reasonably good simulant. There is an indication that a single cycle procedure could be satisfactory if the right solid colored soil component were used.

Neither carbon black nor the mixture of procedure 2 is completely satisfactory. It is probable that a more detailed knowledge of the colored solid components of the "natural" soil would be useful in this regard. Of the two solid soils used in the multi-cycle procedures air conditioner dirt appears to be a more realistic simulant than vacuum cleaner dirt. This may, however, be true only for the type of soil accumulated in these particular bundle tests. The ratio of oily soil to solid soil in the mixture appears to be a factor of relatively minor importance, as evidenced by the similarity of the effects of procedures 4 and 5. A large proportion of the oily portion of a high-oil soil remains in the fabric even after most of the colored soil components have been washed out. The excess oil may have an adverse influence on the consistency of the test, particularly on its sensitivity to variations in hardness and concentration, as evidenced in Table BG7. Detergent concentration and water hardness have less effect on detergent ranking than might be expected. The overlaps and crossovers in ranking are not unexpected in the single cycle tests. In the multi-cycle tests they indicate that more cycles are needed, even after significant differences among the detergents begin to appear.

Since the bundle test is multi-cycle it is logical to expect that a multi-cycle test would be the best simulant. The data support this view, and in the present state of the testing art multi-cycle tests appear more reliable than single-cycle. The most important factor in simulation appears to be the colored components of the solids in the soiling mixture. These should ideally be identical in chemical composition and in particle size range to the colored components of the natural soil deposited on laundry. There have been many excellent studies on soil composition, but few reports we are aware of on the nature of the soil that causes gradual graying of laundry on repeated usage-washing cycles. More work in this field would obviously be a valuable contribution. In the meanwhile the air conditioner soil of procedure 3 (rating AHAM over D and M) and the vacuum cleaner soil of procedure 4 (rating D over M) appear to offer the closest and most consistent simulation of the bundle test.

H. One of the important questions in modern practical detergency is the effect of permanent press treatment on the washability of cotton and polyester fabrics, and on blends of these two fibers. Since this laboratory is equipped to apply permanent press finishes under controlled conditions, a study could be and was undertaken to determine this effect. Five fabrics were used in the study: an unfinished cotton (Testfabrics #400 M print cloth); an unfinished Dacron batiste (Testfabrics #707); these same two fabrics with a permanent press finish applied as described below, and purchased 50:50 cotton-polyester Cannon sheets permanent press finish (the same "blend fabric" used in most of the presently reported studies. The finish applied to the cotton and Dacron was as follows:

Permafresh 114B	6% ow fabric
Velvamine 732	.33% ow fabric
Catalyst KR	25% ow resin
Triton X-100	2% ow bath
Water to 100%	

This mixture was applied by padding to 70% wet pick up. The fabric was dried at 150°F 5 to 10 minutes; pressed at 320°F, and cured at 340°F for 5 minutes. It is noteworthy that this treatment contains no soil-release agent.

The soiling and laundering of these fabrics was carried out by both the Spangler multi-cycle and the Colgate single cycle procedures. The detergent in all cases was AATCCWOB and the water was 200 ppm hardness, 4 Ca:1Mg. In the Spangler tests the detergent concentration was 0.3%.

The Colgate tests, as always, were run as detergency v. concentration series.

The results of the Spangler tests are shown in Figure 37-39. The difference between the green reflectance values and the whiteness indicates that the permanent press treatment tends to alter the hue of the fabric slightly. This alteration is noticeable to the eye on Dacron but not on cotton. The slope of the curves in Figures 38 and 39 indicate that the treatment makes the fabric less prone to soil accumulation. The commercial blend fabric (Figure 39) loses whiteness more rapidly than any of the other four fabrics.

The results of the Colgate tests are diagrammed in Figures 40-45. They show the soil pick up during swatch preparation as well as the washing behavior. The permanent press finish obviously makes cotton much more prone to pick up soil than it is in the unfinished state. It also raises the minimum effective concentration (MEC) of the detergent, i.e. the concentration necessary to reach the detergency plateau. Treatment has relatively little effect on the soil pick up of the Dacron, but it does make the Dacron more difficult to clean. The blend fabric (Figures 44 and 45) behaves as expected like a mixture of treated Dacron and treated cotton. The fact that the absolute reflectance level of the blend fabric is higher than that of the laboratory treated fabrics is ascribed to a different finishing treatment. It is probable that a soil release ingredient was included in the treating formula used on the commercial fabric.

It is generally believed among textile chemists that the permanent press finish has little effect on the polyester component of a blend fabric because the aminoplast prepolymer does not penetrate to the fiber interior. The present study indicates that sufficient final polymer remains adherent to the polyester's surface to change its soiling and washing characteristics very markedly. The results indicate, in fact, that this typical permanent press finish affects the polyester fully as much as the cotton with regard soilability and launderability.

Table BG1

INSTRUMENTAL REFLECTANCES OF LAUNDERED PILLOWCASES AFTER SIX CYCLES IN BUNDLE TEST

	G	Delta G AHAM	Whiteness	Delta Whiteness AHAM	Yellowness	Delta Yellowness AHAM
AHAM durapress	83.8	0	76.2	0	.01	0
D durapress	84.0	-0.2	76.0	0.2	.01	0
AHAM cotton	90.1	0	76.5	0	.03	0
D cotton	90.4	-0.3	75.2	1.3	.04	.01
AHAM durapress	83.3	0	71.3	0	.02	0
M durapress	83.0	0.3	67.8	3.5	.03	.01
AHAM cotton	88.9	0	66.1	0	.06	0
M cotton	87.6	1.3	59.6	6.5	.08	.02

Table BG2

TERGOTOMETER SOIL REMOVAL VALUES
Cotton, 0.2%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches	% on washed swatches	Delta vs AHAM
			Detergent D			
1	3.10	1.90	.003	1.19	.75	-.03
2	-.20	-.50	.002	7.76	2.61	.03
			Detergent M			
1	1.40	.60	.003	1.19	1.01	-.29
2	-1.60	-.80	-.002	7.76	2.68	-.04
			Detergent AATCC #124			
1	.60	.10	.003	1.19	.56	.16
2	0	0	.004	7.76	2.64	0

Table BG2A

TERGOTOMETER REDEPOSITION VALUES
Cotton, 0.2%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches	% on washed swatches	Delta vs AHAM
			Detergent D			
1	-5.6	-5.2	.004			
2	-0.6	-1.3	.003			
			Detergent M			
1	-3.8	-3.2	.002			
2	-0.3	0.3	.001			
			Detergent AATCC #124			
1	-2.8	-1.5	.003			
2	-0.7	0.1	.002			

Table BG3

TERGOTOMETER SOIL REMOVAL VALUES
Durapress, .2%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
				% on soiled swatches	% on washed swatches	Delta vs AHAM
	G	Whiteness	Yellowness			
			Detergent D			
2	11.6	9.6	.001	7.37	2.35	-.39
			Detergent M			
2	7.80	6.70	-.001	7.37	2.58	-.62
			Detergent AATCC #124			
2	-1.50	-1.30	-.001	7.37	1.82	.14

Table BG3A

TERGOTOMETER REDEPOSITION VALUES
Durapress, 0.2%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches	% on washed swatches	Delta vs AHAM
			Detergent D			
2	.3	.4	.000			
			Detergent M			
2	-1.2	-0.8	.000			
			Detergent AATCC #124			
2	-0.3	-1.0	.004			

Table BG4

TERGOTOMETER SOIL REMOVAL VALUES
Cotton, 0.3%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches Swatches	% on washed swatches Swatches	Delta vs AHAM
			Detergent D			
3	-.80	1.20	-.006	4.74	3.29	.91
4	-4.40	-5.00	.011	1.44	.39	.18
5	-4.80	-4.70	.009	5.69	3.39	-1.60
			Detergent M			
3	-.90	1.90	-.010	4.74	3.53	.67
4	-3.30	-3.00	.006	1.44	.45	.12
5	-4.40	-4.10	.007	5.69	3.37	-1.58
			Detergent AATCC #124			
3	-.50	1.00	0	4.74	3.07	-.87
4	-1.50	.30	.002	1.44	.61	-.04
5	-1.70	.30	.001	5.69	2.81	-1.02

Table BG4A

TERGOTOMETER REDEPOSITION VALUES
Cotton, 0.3%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches	% on washed swatches	Delta vs AHAM
			Detergent D			
3	-0.5	-0.3	-.001			
4	-1.4	-2.9	.007			
5	-1.5	-3.0	.006			
			Detergent M			
3	-0.4	-0.3	-.001			
4	-1.2	-2.2	.006			
5	-1.2	-1.4	.001			
			Detergent AATCC #124			
3	-0.6	1.2	.001			
4	-1.5	0.7	.002			
5	-1.3	2.2	-.004			

Table BG5

TERGOTOMETER SOIL REMOVAL VALUES
Durapress, 0.3%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches	% on washed swatches	Delta vs AHAM
			Detergent D			
3	3.30	4.60	-.010	4.24	1.97	-.26
4	-2.50	-4.40	.012	1.88	.65	0
5	-3.20	-4.00	.010	4.30	1.99	-.42
			Detergent M			
3	2.40	4.30	-.010	4.24	1.60	.11
4	-2.80	-4.80	.013	1.88	.65	0
5	-3.00	-3.00	.006	4.30	1.84	-.27
			Detergent AATCC #124			
3	-.10	-.80	.002	4.24	1.61	.10
4	-.10	-.50	.002	1.88	.72	-.07
5	-.60	-1.60	.006	4.30	1.72	-.15

Table BG5A

TERGOTOMETER REDEPOSITION VALUES
Durapress, 0.3%, Tap Water

Col. 1	2	3	4	5	6	7
Procedure No.	Delta Values Reflectance vs AHAM			Alcohol Extractable Material		
	G	Whiteness	Yellowness	% on soiled swatches	% on washed swatches	Delta vs AHAM
			Detergent D			
3	-.1	1.0	-.003			
4	.3	-.8	.004			
5	.4	-1.0	.005			
			Detergent M			
3	0	-.4	.001			
4	.1	-.9	.003			
5	.2	-.1	.002			
			Detergent AATCC #124			
3	0	.2	0			
4	-.1	-.5	.001			
5	0	-.9	.003			

Table BG6

RANKINGS OF DETERGENTS IN DIFFERENT WASHING PROCEDURES

	Whiteness Ranking of Soiled Swatches			
Procedure	0.2 %, Tap Water		0.3 %, Tap Water	
	Cotton	DP	Cotton	DP
Bundle	AHAM D M	AHAM D M		
1	AHAM AATCC M D		AHAM M AATCC D	
2	M D AATCC AHAM	AATCC AHAM M D	AHAM D AATCC M	AATCC AHAM M D
3	D M	M D	AHAM AATCC D M	AATCC AHAM M D
4	D M	M D	D M AHAM AATCC	M D AATCC AHAM
5	D M	M D	D M AHAM AATCC	D M AATCC AHAM

Table BG7

WHITENESS RANKINGS OF SOILED SWATCHES IN PROCEDURES 1 and 2

Procedure	0.1 %, Tap Water		0.1 %, Harl Water		0.2 % Hard Water		0.3 %, Hard Water	
	Cotton	DP	Cotton	DP	Cotton	DP	Cotton	DP
1	AHAM AATCC M D		AATCC AHAM M D		AATCC AHAM M D		AATCC AHAM M D	
2	M D AATCC AHAM	AATCC AHAM M D	M AATCC D AHAM	M AATCC D AHAM	M AHAM AATCC D	AATCC AHAM M D	AHAM AATCC M D	AATCC AHAM M D

Table BG8

WHITENESS RANKINGS OF SOILED SWATCHES IN PROCEDURES 3, 4 and 5
0.3%; Hard Water

Procedure	Cotton	DP
3	AHAM]	AATCC]
	[AATCC]	AHAM]
	[M	M
	[D	D
4	[D	D
	[M	M
	AHAM]	AATCC]
	AATCC]	AHAM]
5	[D	[D
	[M	[M
	AATCC]	AATCC]
	AHAM]	AHAM]

Table BG9

WHITENESS RANKINGS OF SOILED SWATCHES
DETERGENTS M and D IN PROCEDURES 3, 4 and 5

Procedure	0.1 %, Tap Water		0.1 %, Hard Water		0.2 %, Hard Water		0.3 %, Hard Water	
	Cotton	DP	Cotton	DP	Cotton	DP	Cotton	DP
3	⎡M ⎣D	M D	⎡M ⎣D	M D	⎡M ⎣D	M D	⎡M ⎣D	M D
4	D M	⎡M ⎣D	⎡D ⎣M	⎡D ⎣M	⎡D ⎣M	⎡D ⎣M	⎡D ⎣M	D M
5	D M	M D	⎡M ⎣D	M D	⎡D ⎣M	M D	⎡D ⎣M	⎡D ⎣M

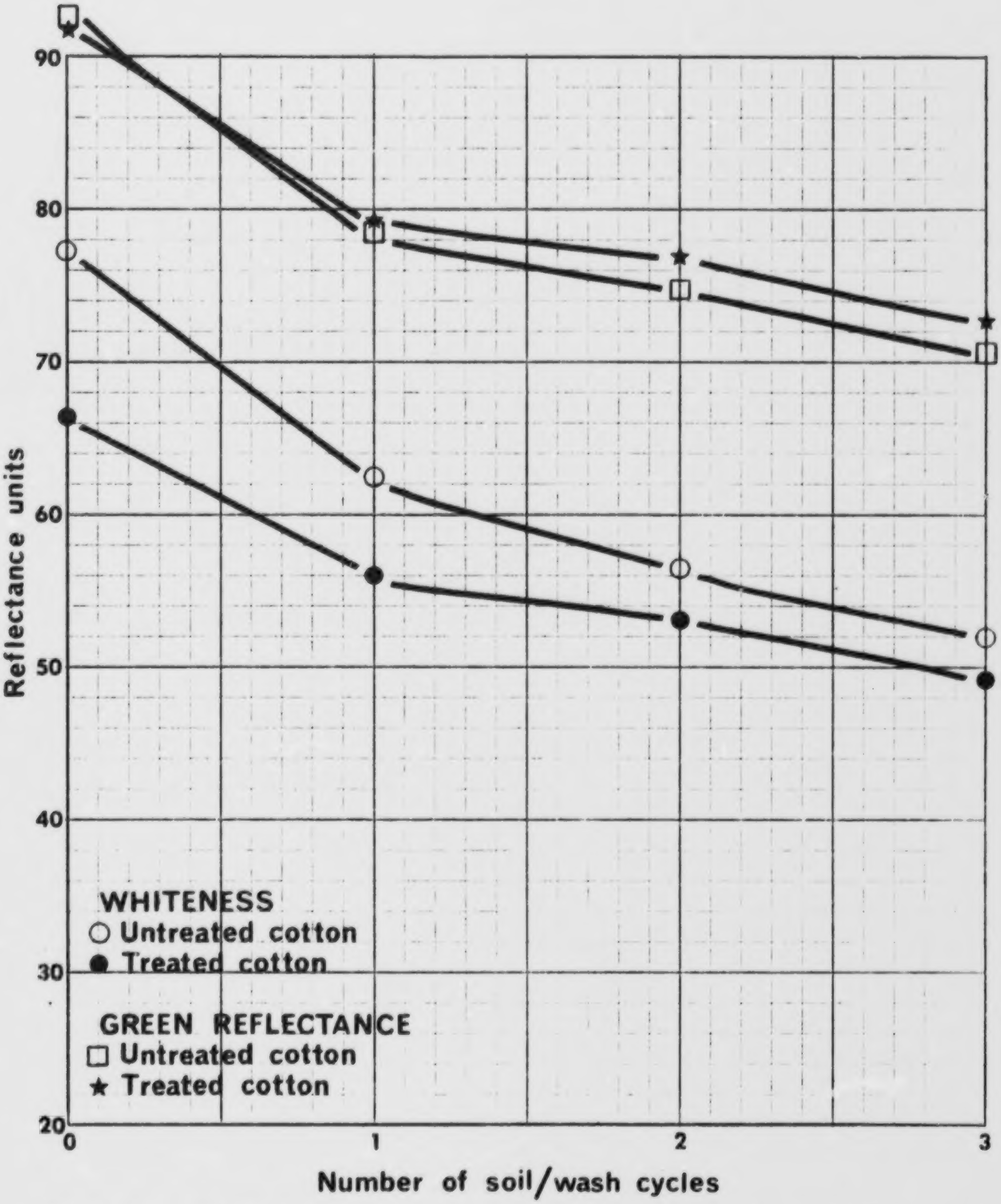


Figure 37. Fabric finish study. Spangler multicycle. 200 ppm water. AATCCWOB 0.3%. Cotton.

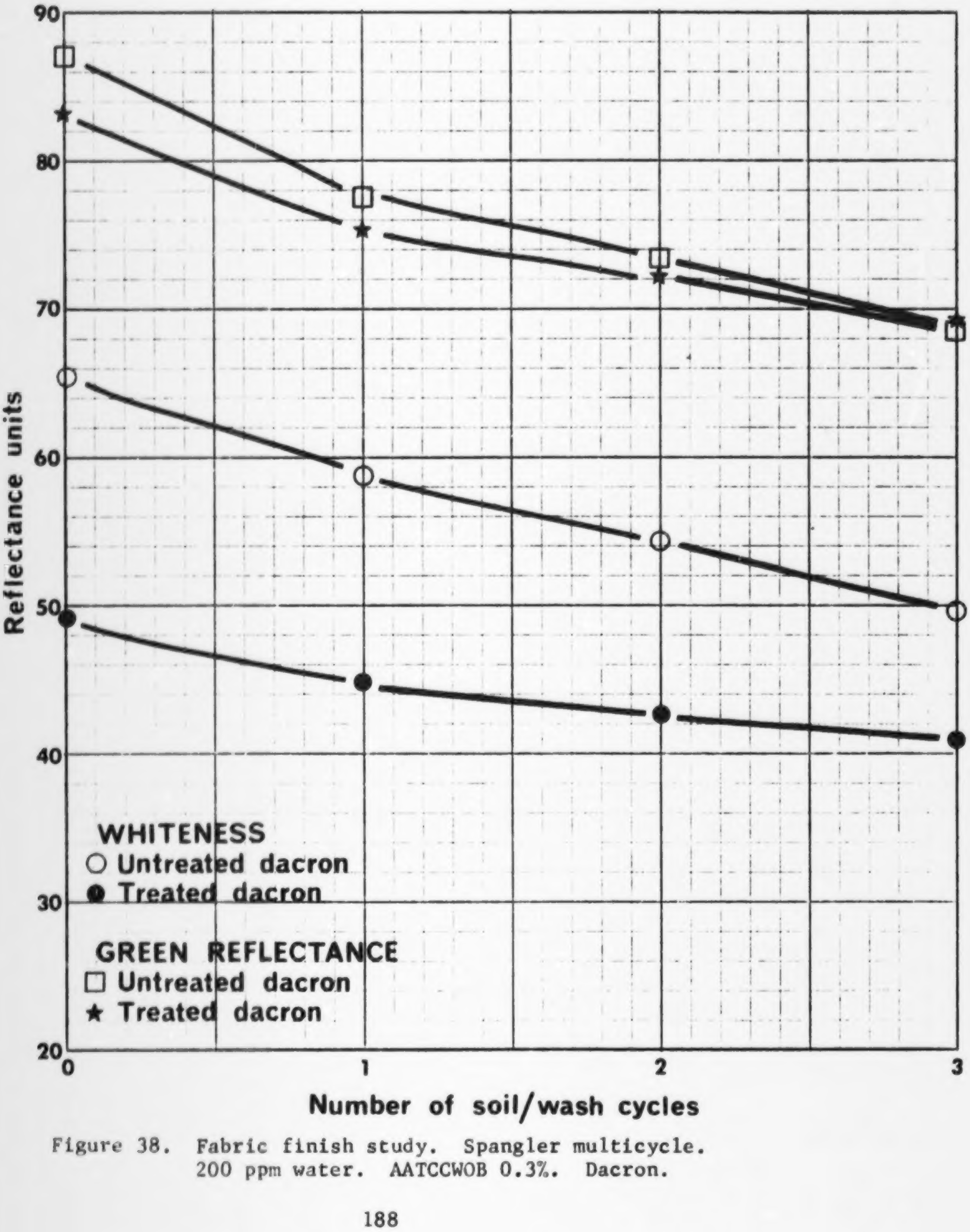


Figure 38. Fabric finish study. Spangler multicycle. 200 ppm water. AATCCWOB 0.3%. Dacron.

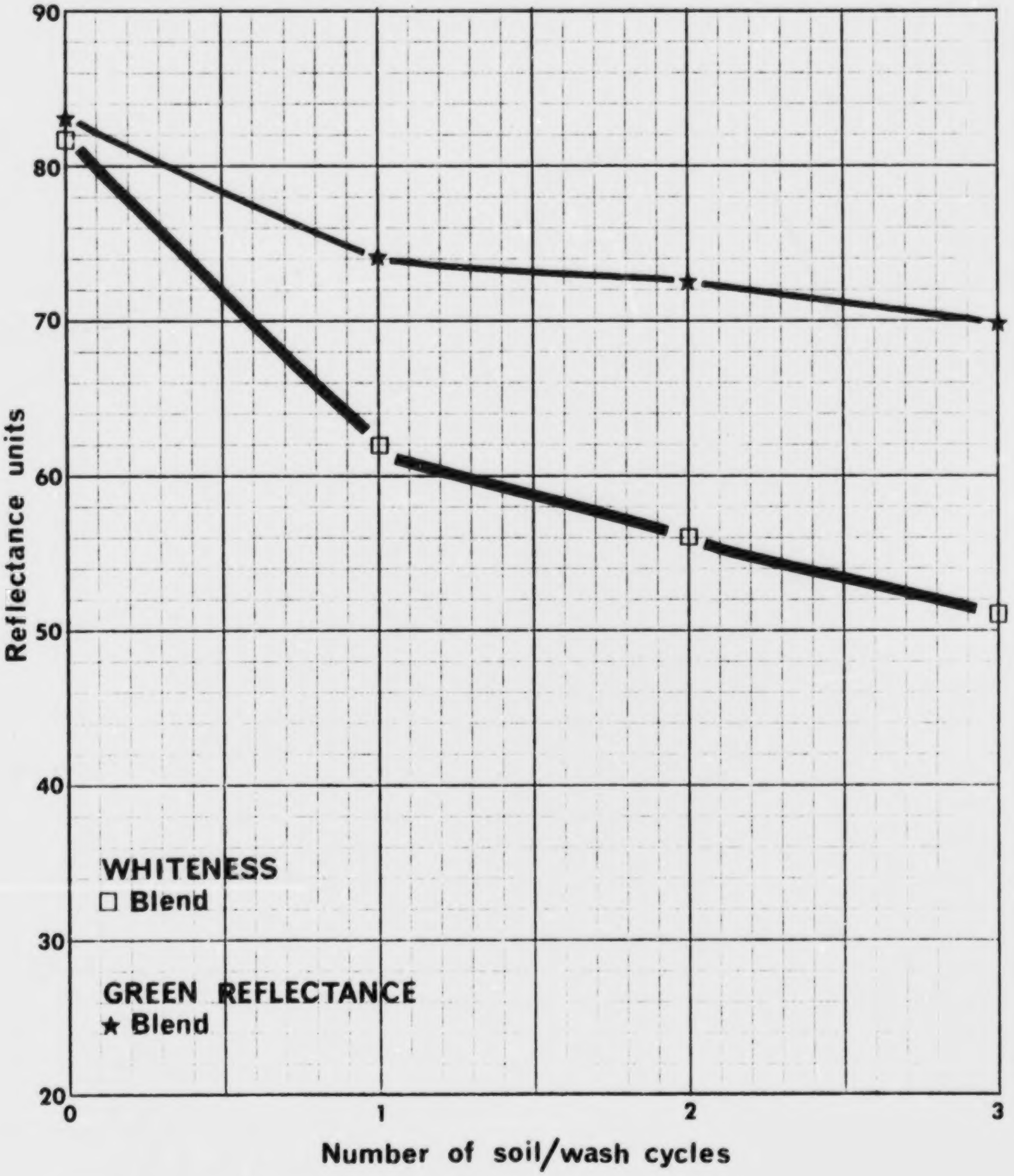


Figure 39. Fabric finish study. Spangler multicycle. 200 ppm water. AATCCWOB 0.3%. Blend fabric.

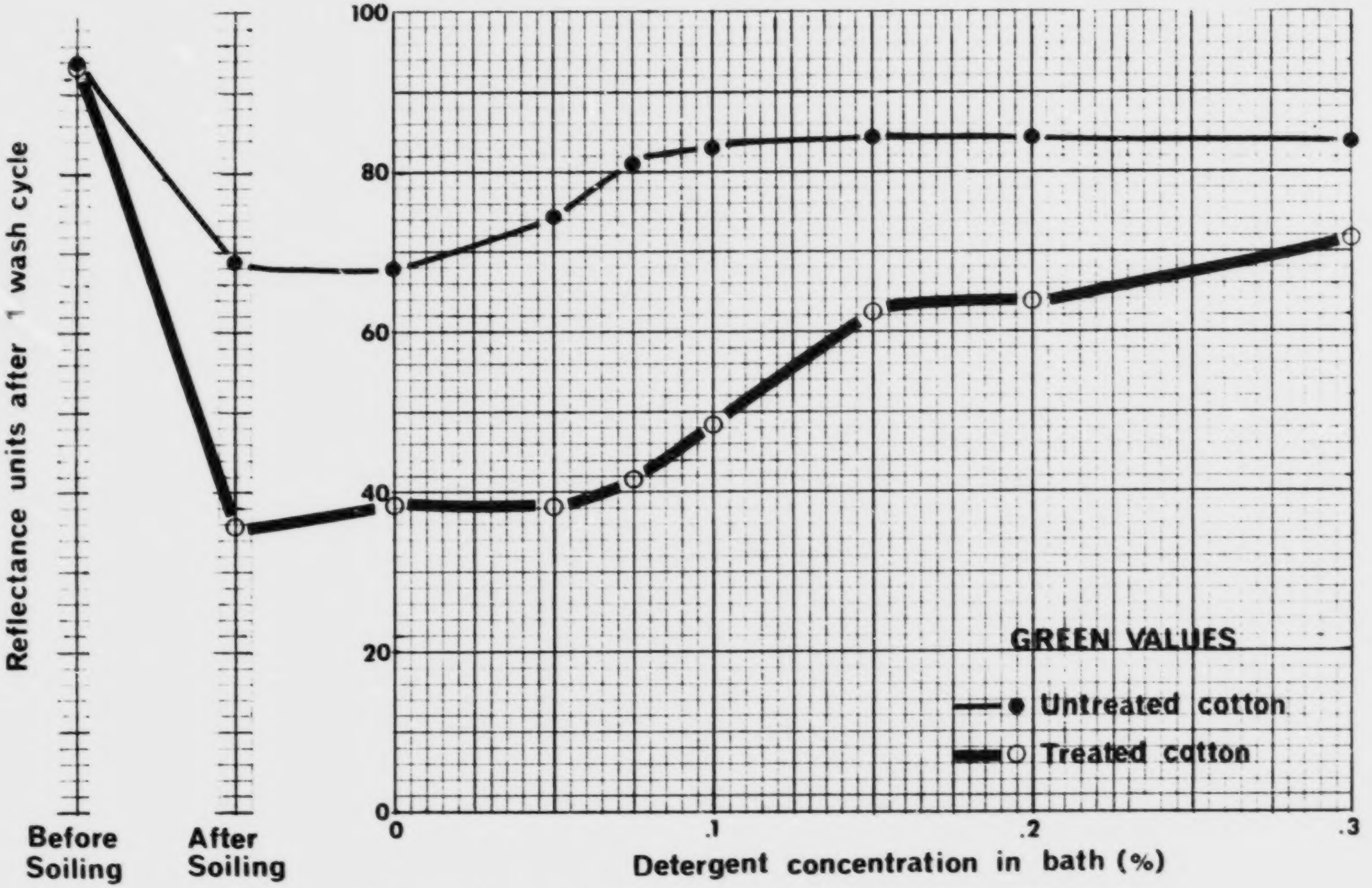


Figure 40. Fabric finish study. Colgate soil. 200 ppm water. AATCCWOB. Cotton. Green reflectance values.

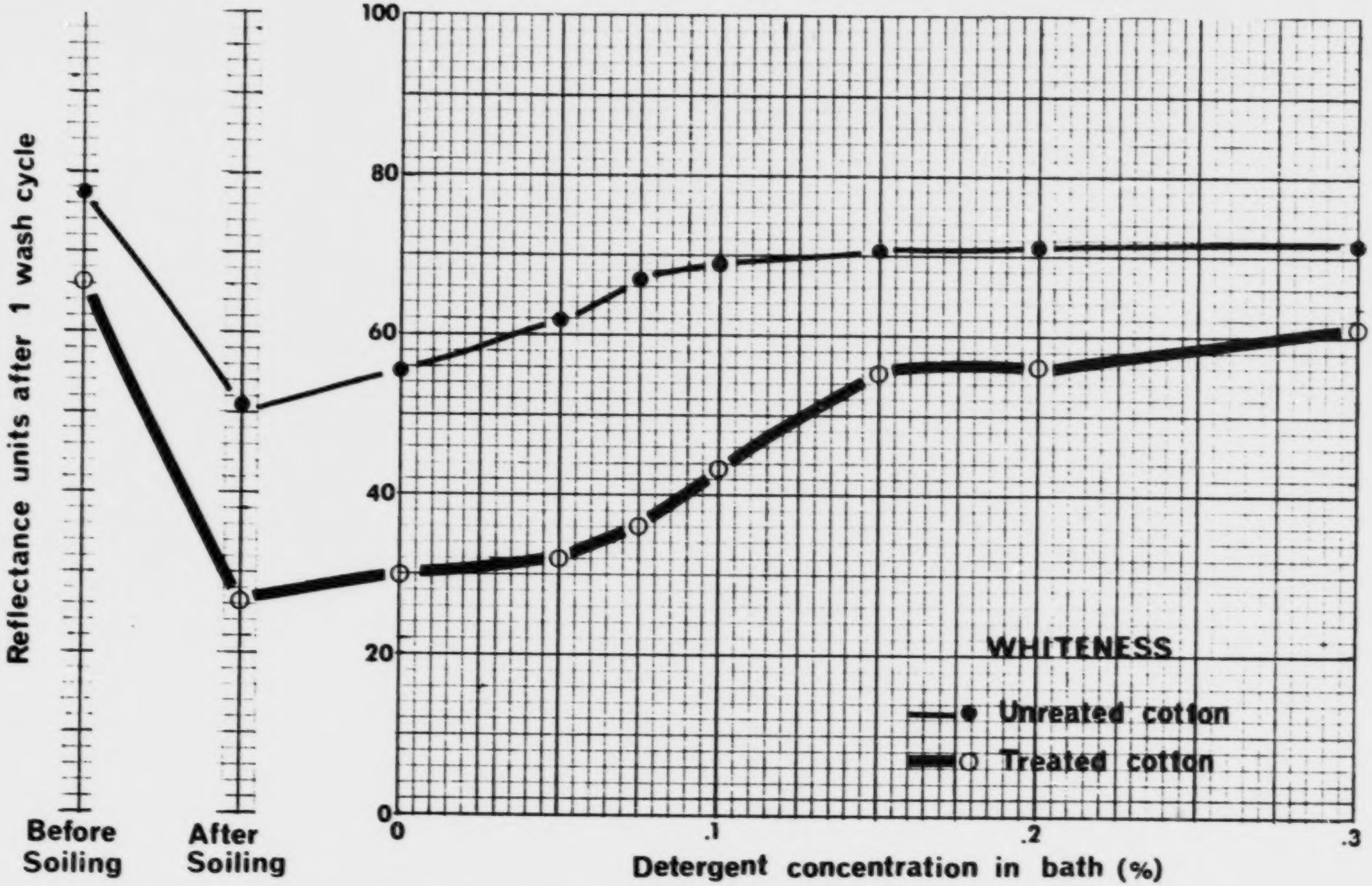


Figure 41. Fabric finish study. Colgate soil. 200 ppm water. AATCCWOB. Cotton. Whiteness values.

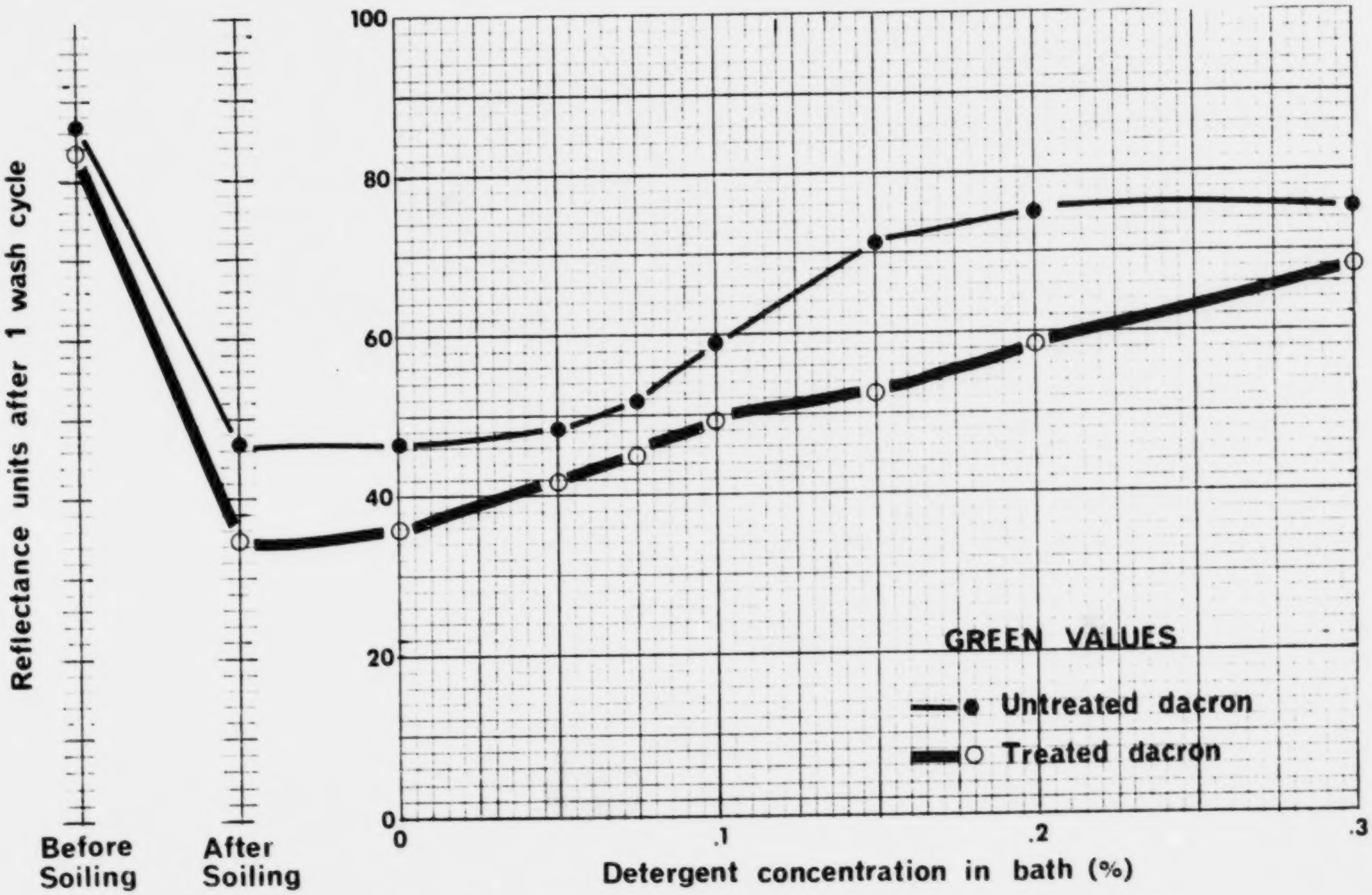


Figure 42. Fabric finish study. Colgate soil. 200 ppm water. AATCCWOB. Dacron. Green reflectance values.

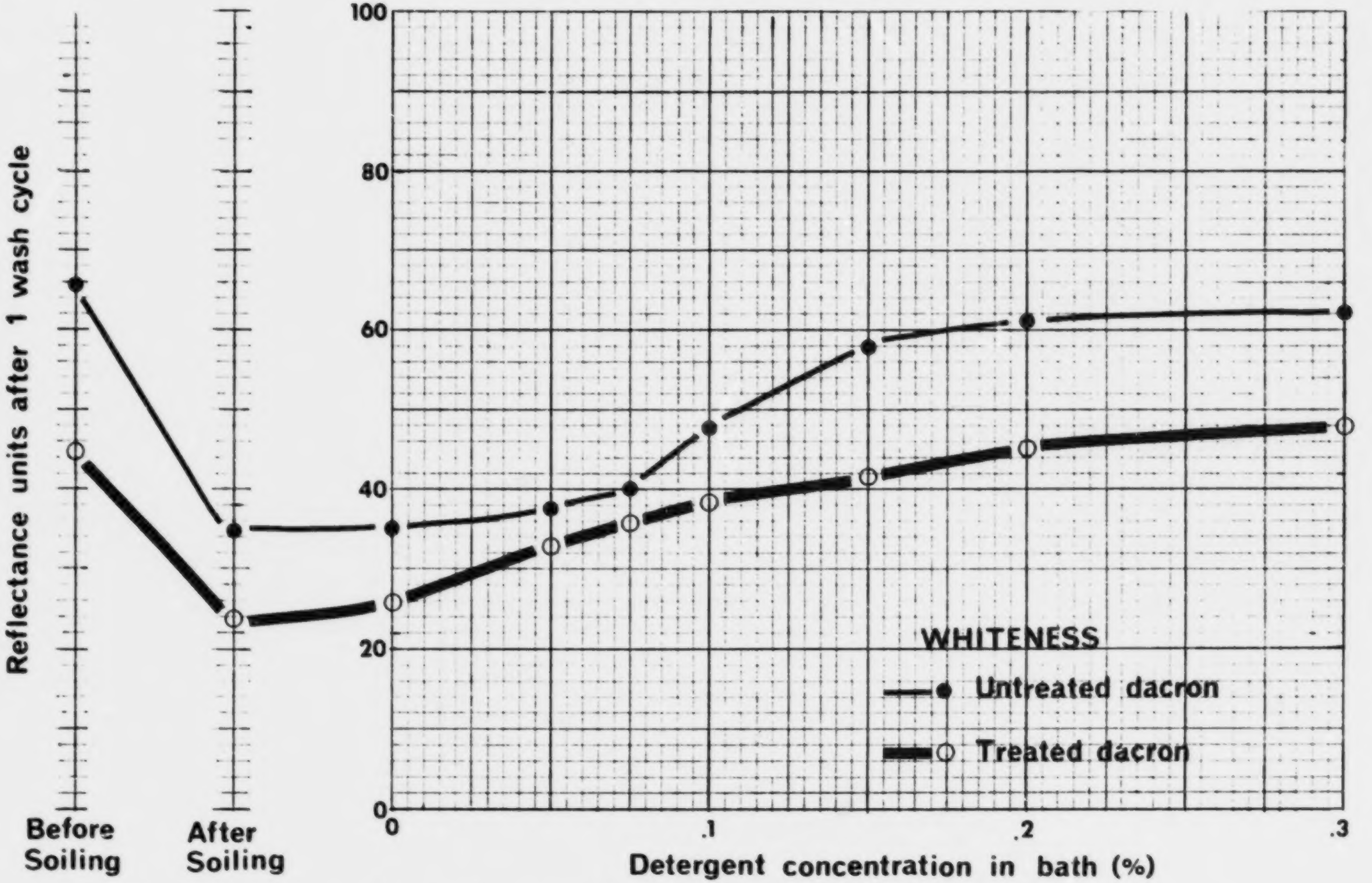


Figure 43. Fabric finish study. Colgate soil. 200 ppm water. AATCCWOB. Dacron. Whiteness values.

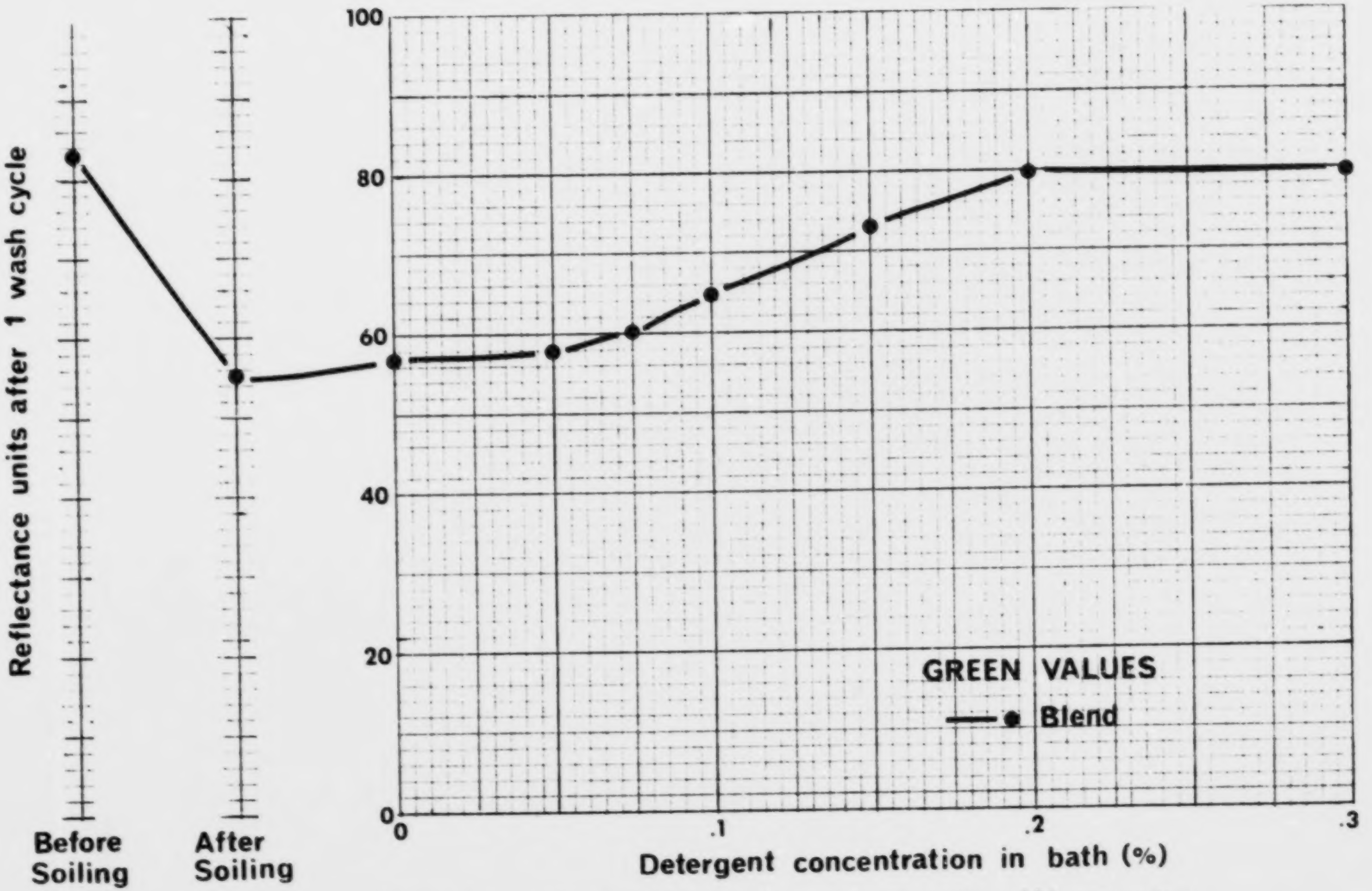


Figure 44. Fabric finish study. Colgate soil. 200 ppm water. AATCCWOB. Blend fabric (commercial permanent press finish). Green reflectance values.

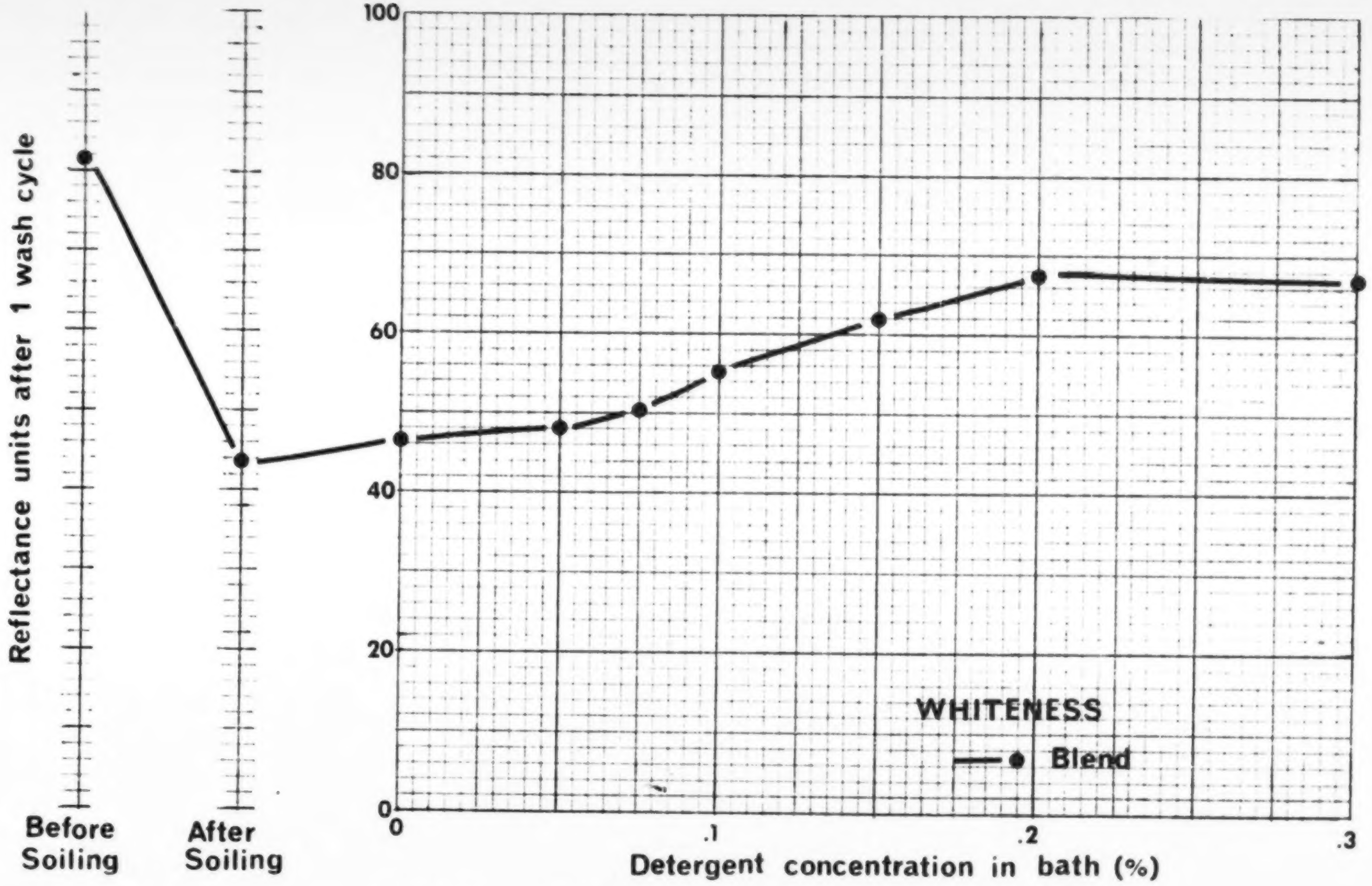


Figure 45. Fabric finish study. Colgate soil. 200 ppm water. AATCCWOB. Blend fabric (commercial permanent press finish). Whiteness values.

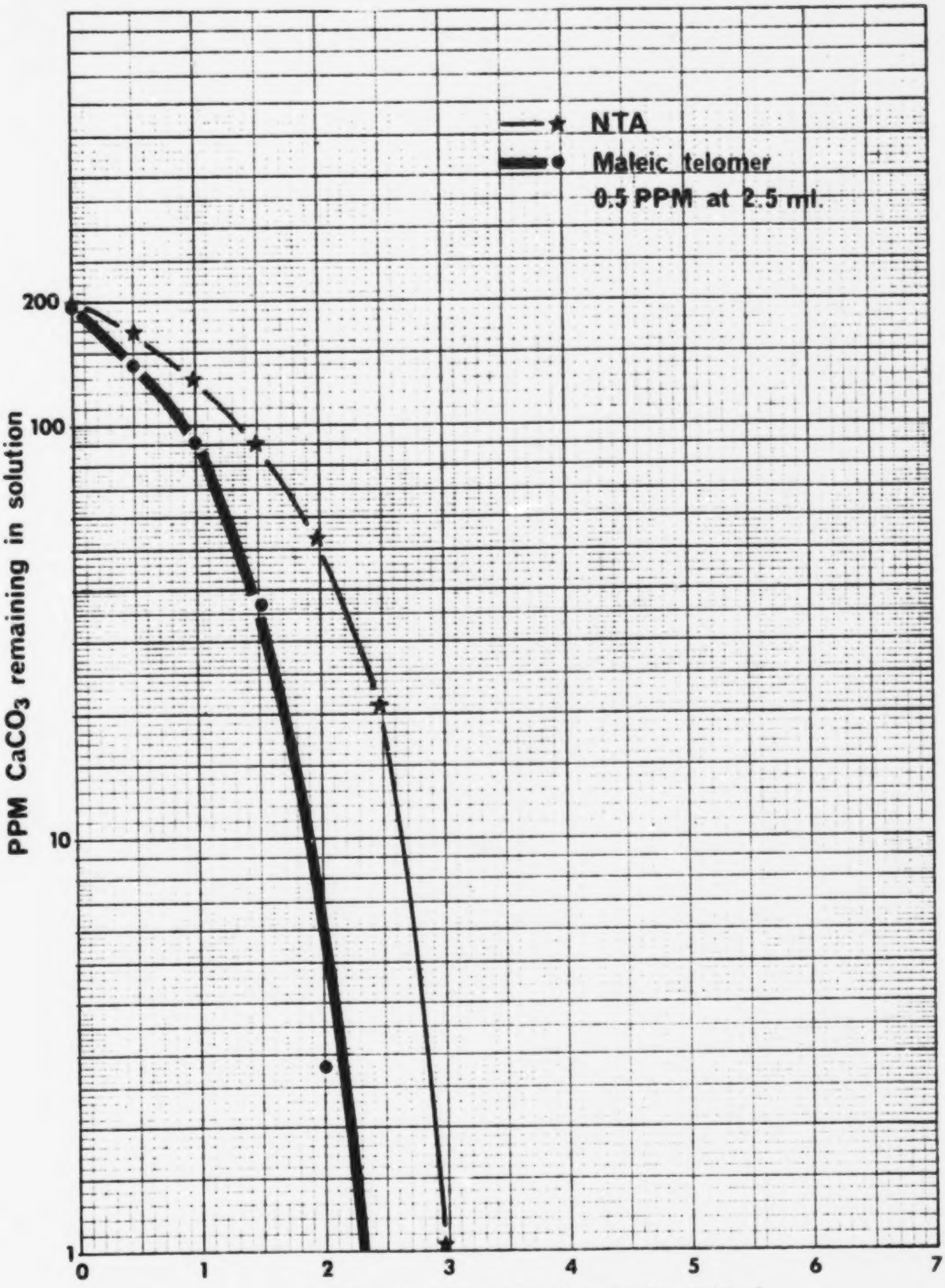


Figure 46. Chelation curves of typical strong, high efficiency chelants, NTA and maleic acid telomer.

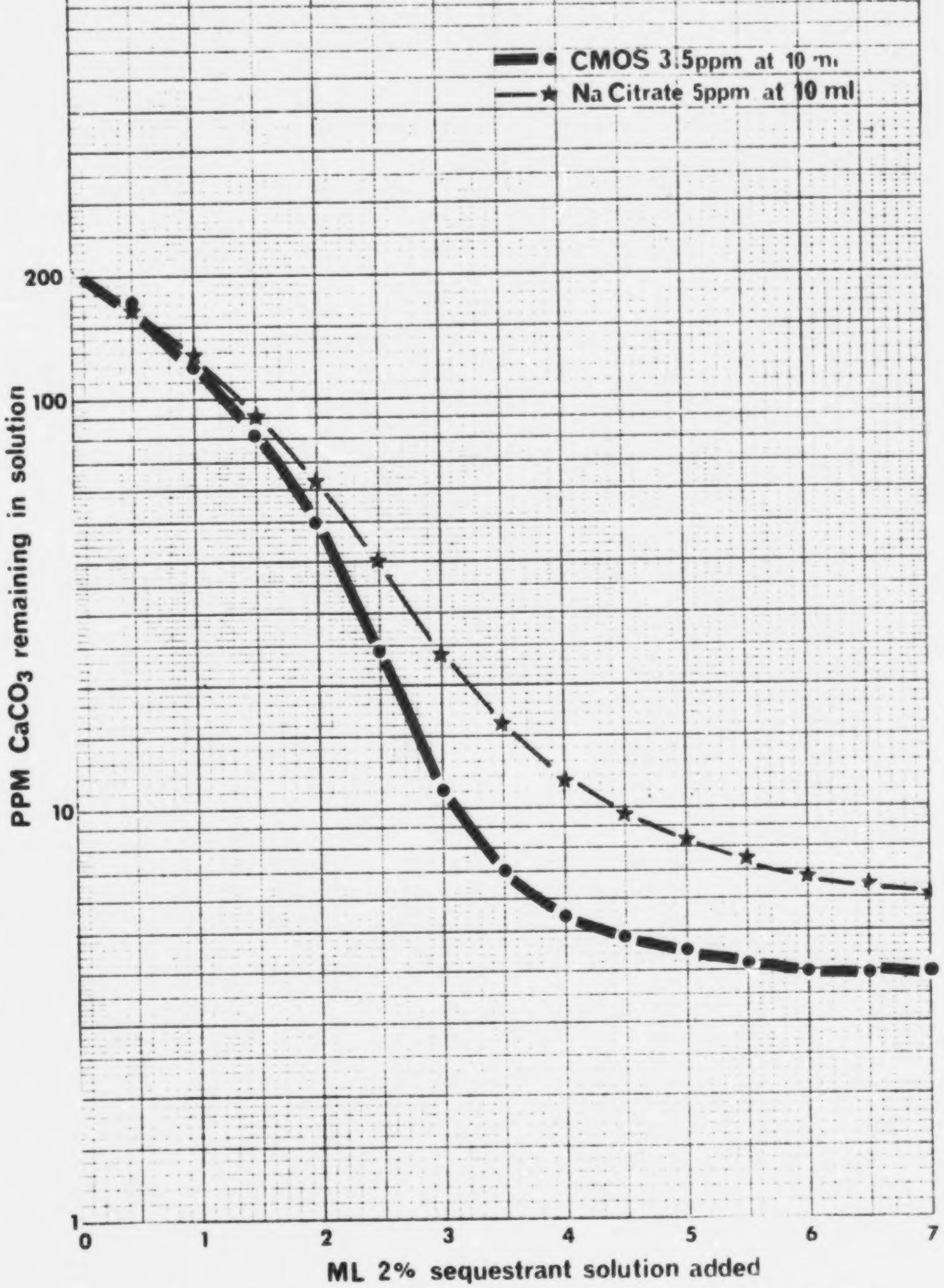
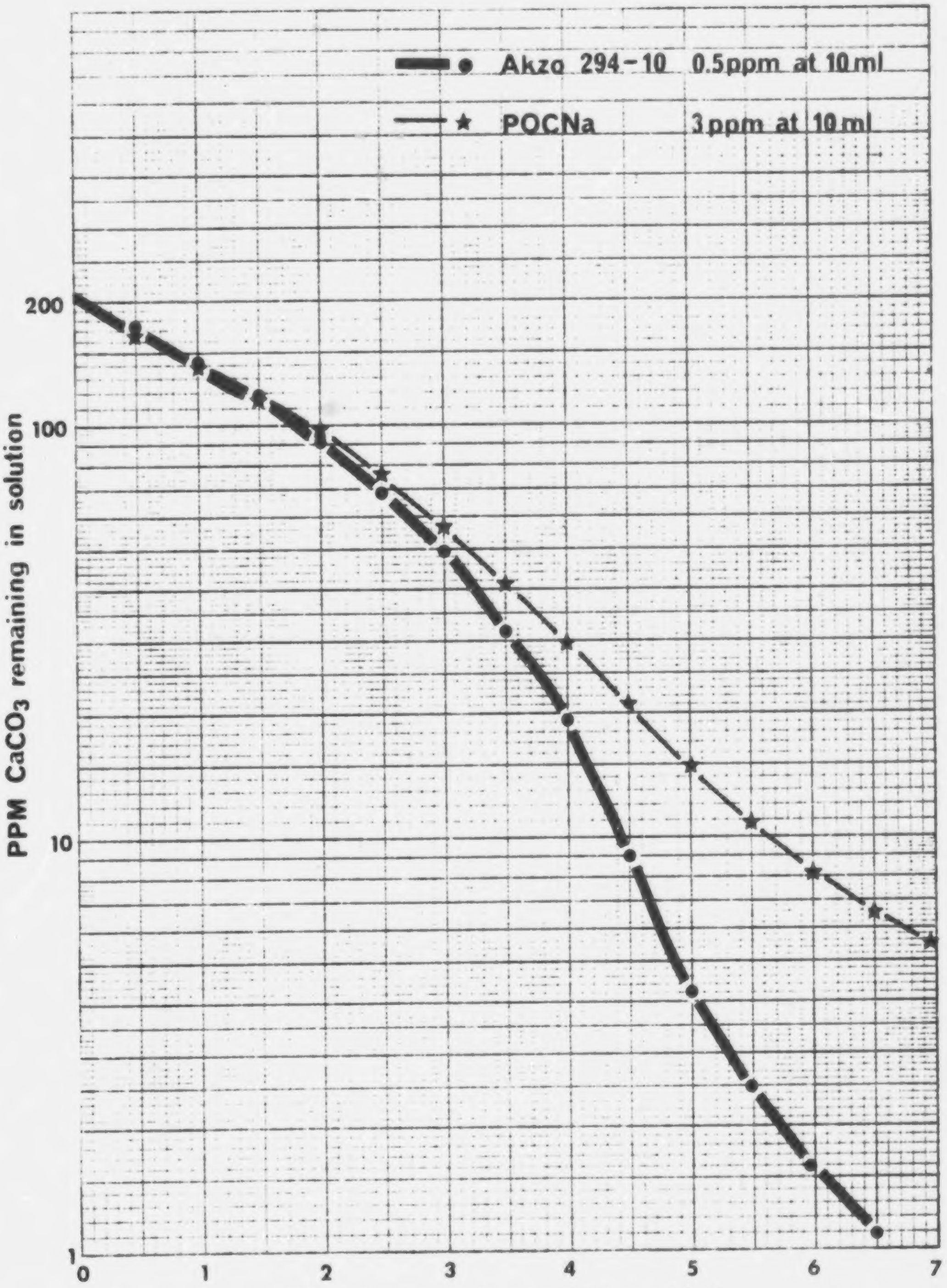


Figure 47. Chelation curves of weak, moderate efficiency chelants, Na citrate and CMOS.



igure 48. Low efficiency polymeric chelants. Akzo 294-10 moderately strong, POCNa moderately weak.

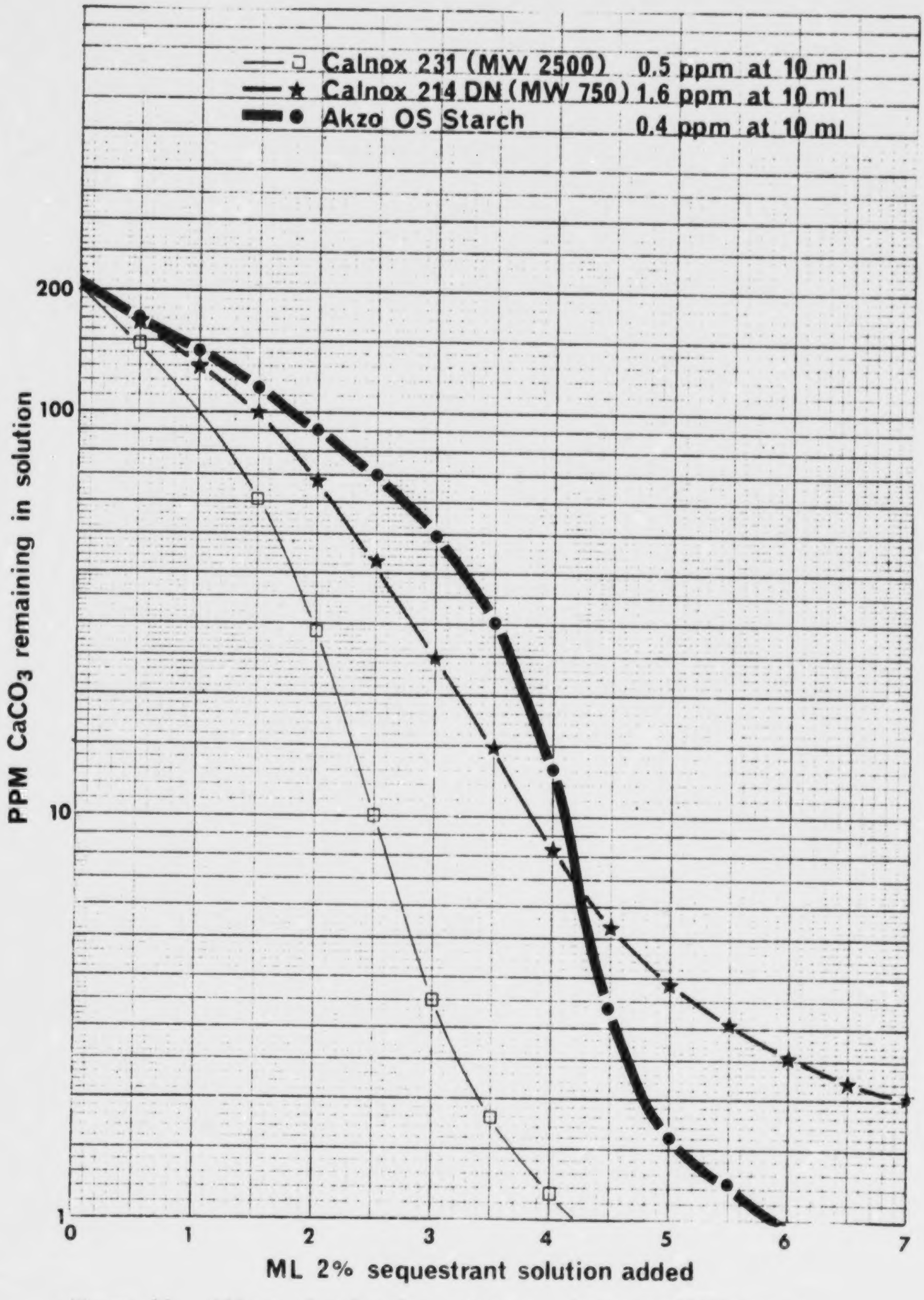


Figure 49. Effect of molecular weight on chelating behavior in polyacrylic acids (Calnox). Akzo OS starch typical of low efficiency moderate strength polymeric builders.

APPENDIX C

CODE LIST OF MATERIALS

Code No.	Type	Identity
20-138	Fatty alcohol ethoxylate surfactant	Plurafac A-38 (Wyandotte Chem. Corp.
20-141	Polymeric builder	Experimental 18507-27 (Celanese Chem. Co.)
20-144	Hydroxylated nonionic surfactant	Ninol AA62 (Stepan Chemical Co.)
20-145	Hydroxylated nonionic surfactant	Nittoester P-1570 (Dai Nippon Sugar Mfg. Co.)
20-146	Low titer soap	
20-147	High titer soap	
20-151	Glucoheptonic acid builder	Seqlene S540 (Pfanstiehl Laboratories, Inc.)
20-152	Citric acid (sodium salt) builder	Pfizer Chemicals Div.
22-155	Alpha olefin sulfonate surfactant	Bioterge AS-35-CL (Stepan Chem. Co.)
26-189	Hydroxylated nonionic surfactant	Experimental compound IL728 (Atlas Chem. Industries, Inc.)
26-191	Hydroxylated nonionic surfactant	Experimental compound IL725 (Atlas Chem. Industries, Inc.)
31-230	Sucrose Hexadecyl Ether	Experimental compound 1303-23, GRI

Appendix C (Continued)

Code No.	Type	Identity
32-237	Commercial detergent extract	Alcohol soluble material (surfactant) extracted from Tide XK
34-249	Alkyl aryl sulfonate (LAS)	Ultrawet K Special (Arco Chem. Co.)
36-276	Experimental formulation, GRI	40 Hi titer soap/15 Alfonic 1218-60/8G/1/36
36-277	Experimental formulation, GRI	40 Low titer soap/15 Alfonic 1218-60/8G/1/36
36-278	Experimental formulation, GRI	20 Low titer soap/15 Alfonic 1218-60/8G/1/36/+20 H_2O
38-279	Diglycollic acid (Na salt)	Biosoft SB-1 (Stepan Chem. Co.)
38-282	Commercial detergent	Concern (H.T.Development, Inc.) Purchased 1970
40-309	Diglycollic acid (Na salt)	Experimental compound SN1048 (Celanese Chem. Co.)
40-310	Polymeric builder	Gantrex AN-119 (GAF Corp.)
40-312	SAND, Monoacidamide of nitrilotriacetic acid	(Bethlehem Steel Co.)
40-332	Ether carboxylate anionic surfactant	Experimental compound 1245 (Dow Chem. Co.)
42-348	Sulfo zwitterionic surfactant	Sulfobetaine DLM (Textilana Corp.)
42-350	Sulfobetaine zwitterionic surfactant	Sulfobetaine TA75 (Textilana Corp.)

Appendix C (Continued)

Code No.	Type	Identity
42-353	Sulfo zwitterionic surfactant	Sulfobetaine DP (Textilana Corp.)
43-64	Commercial detergent, high carbonate type	Sears Laundry Detergent - Phosphate Free
43-65	Polymeric builder	Versicol E7 (Allied Colloid Mfg. Co.)
43-67	Fatty alcohol ethoxylate surfactant	Arosurf 63PE16 (Ashland Chemical Co.)
43-74	Polymeric builder	Experimental 18507-48 (Celanese Chem. Co.)
43-83	Hydroxylated nonionic surfactant	Experimental surfactant 31-43 (Northern Regional Laboratory USDA)
46-356	Carboxy zwitterionic surfactant	Velvetex BC (Textilana Corp.)
46-357	Carboxy zwitterionic surfactant	Tegobetaine C (Goldschmidt Chemical Div.)
48-374	Amine oxide surfactant	Aromox C/12W (Armour Industrial Chem. Co.)
51-91	Alkane sulfonate anionic surfactant	Hostapur SAS-60 (American Hoechst Corp.)
51-93	Fatty alcohol ethoxylate nonionic surfactant	Alfonic 1618-65 (Continental Oil Co.)
51-100	Fatty alcohol ethoxylate nonionic surfactant	Arosurf 63-E15 (Ashland Chem. Co.)
51-101	Fatty alcohol ethoxylate nonionic surfactant	Arosurf 42-E12 (Ashland Chem. Co.)

Appendix C (Continued)

Code No.	Type	Identity
51-104	Fatty alcohol ethoxylate nonionic surfactant	Plurafac B-26 (Wyandotte Chem. Co.)
51-105	Fatty alcohol ethoxylate nonionic surfactant	Plurafac D-25 (Wyandotte Chem. Co.)
54-431	Sulfo zwitterionic surfactant	Miranol CS Conc. (Miranol Chem. Co.)
54-433	Sulfo zwitterionic surfactant	Miranol DS (Miranol Chem. Co.)
56-445	Hydroxyethylimino diacetic acid	(Bethlehem Steel Co.)
58-466	Polymeric builder	Experimental Product 335 (Amicon Corp.)
58-467	Polymeric builder	Experimental Product 933 (Amicon Corp.)
58-471	Ether sulfate anionic surfactant	Steol 4N (Stepan Chem. Co.)
60-486	Ether carboxylate anionic surfactant	Experimental compound 7-26A (Dow Chem. Co.)
62-491	Ether sulfate anionic surfactant	Alfonic 1412-5 (Continental Oil Co.)
62-492	Ether sulfate anionic surfactant	Experimental compound 1218-EO-50-S (Continental Oil Co.)
66-530	Carbohydrate type polymeric builder	Dicarboxyl starch (Lever Bros.)
66-532	Polymeric builder	Experimental detergent builder S-10244-137-1 (American Cyanamid Co.)

Appendix C (Continued)

Code No.	Type	Identity
66-533	Polymeric builder	Experimental detergent builder S-10244-137-2 (American Cyanamid Co.)
66-541	Monomeric builder, carboxylic acid type	Experimental compound SN1152 (Celanese Chemical Co.)
68-108	Sulfo ampholytic surfactant U.S. Patent 3,084,187	GRI experimental compound #1303-6 (GRI)
68-109	Sulfo ampholytic surfactant U.S. Patent 3,084,187	GRI experimental compound #1303-7 (GRI)
68-127	Fatty alcohol ethoxylate nonionic surfactant	Alfonic 1218-60 (Continental Oil Co.)
68-134	Fatty alcohol ethoxylate nonionic surfactant	Neodol 25-7 (Shell Oil Co.)
68-558	Alpha olefin sulfonate anionic surfactant	Experimental compound OLS07 (Gulf Research and Dev. Co.)
70-560	Commercial detergent	Amway "L.O.C." Liquid Organic Concentrate (Amway Corp.) Purchased 1971
72-589	Monomeric builder	Monoethanolamine Carbonate (GRI)
74-594	Soap type surfactant	#544-151A Soap/lime soap dispersing agent/builder (Eastern Utilization Research & Dev. Div. USDARS)
74-596	Monomeric builder	DL-tartaric acid (Aldrich Chem. Co.)

Appendix C (Continued)

Code No.	Type	Identity
74-602	Carbohydrate type polymeric builder	Carboxymethyl starch (Northern Regional Research Laboratories USDA)
74-604	Alpha olefin sulfonate anionic surfactant	Bioterge AS40G (Stepan Chemical Co.)
74-606	Monomeric builder	Mellitic acid (Chem. Procurement Laboratories)
76-620	Monomeric builder	Tetrahydrofuran-2,3,4,5-tetracarboxylic acid (Aldrich Chemical Co.)
78-633	Ether carboxylate surfactant	Sandopan DTC (Sandoz)
78-634	Ether carboxylate surfactant	Sandopan DTC 100 (Sandoz)
78-635	Fatty alkyl sulfate anionic surfactant	Dupanol ME Dry (Dupont Co.)
80-647	Monomeric builder	Carboxymethyl oxysuccinic Acid
86-700	Laundry Detergent	Standard Laundry Detergent AATCCWOB from Am. Assoc. Textile Chemists & Colorists
86-704	Carbohydrate builder	Methocel XDL 7823 (Dow Chemical Co.)
86-705	Unidentified carboxylated polymer	Polyelectrolyte NX524 (Nalco Chem.Co.)

Appendix C (Continued)

Code No.	Type	Identity
86-706	Soap type surfactant	ER AF569-144-1 Soap/ lime soap dispersing agent builder (Eastern Utilization Research and Dev. Div. USDARS)
86-707	Soap type surfactant	ER AF569-144-2 Soap/ lime soap dispersing agent builder (Eastern Utilization Research and Dev. Div. USDARS)
86-708	Soap type surfactant	ER AF569-144-3 Soap/ lime soap dispersing agent builder (Eastern Utilization Research and Dev. Div. USDARS)
86-709	Maleic copolymer builder	Experimental compound Maldene 270 (Borg-Worner Co.)
88-722	Laundry detergent	Commercial laundry detergent, purchased Chicago, Ill. 1972--Breeze (Lever Bros.)
88-723	Laundry detergent	Commercial laundry detergent, purchased Chicago, Ill. 1972--Wisk (Lever Bros.)
88-726	Laundry detergent	Commercial laundry detergent, purchased Chicago, Ill. 1972--Ajax (Colgate-Palmolive Co.)

Appendix C (Continued)

Code No.	Type	Identity
90-727	Laundry detergent	Commercial laundry detergent purchased Chicago 1972 -- Cold Power (Colgate-Palmolive Co.)
90-729	Laundry detergent	Commercial laundry detergent Opus (Fenom Corp., Göteborg, Sweden)
90-730	Anionic sulfonate surfactant	Chevron D116 (Standard Oil Co. of California)
92-745	Acrylic builder	Goodrite K732 (B.F.Goodrich Chem. Co.)
92-752	Alkyl aryl sulfonate (LAS)	Conoco C550 (Continental Oil Co.)
94-760		Bioterge TMS (Stepan Chemical Co.)
96-782	Laundry detergent	Commercial laundry detergent - purchased 1973 Era (Proctor & Gamble Co.)
96-783	Laundry detergent	Commercial laundry detergent purchased Miami, Fla. 1973-- Cold Power (Colgate-Palmolive Co.)
96-784	Laundry detergent	Commercial laundry detergent purchased Miami 1973--Tide (Proctor & Gamble)
98-806	Unidentified Polymeric builder	Experimental compound IL 740 (Atlas Chem. Industries, Inc.)

Appendix C (Continued)

Code No.	Type	Identity
98-807	Unidentified polymeric builder	Experimental compound IL741 (Atlas Chem. Industries, Inc.)
100-821	Unidentified polymeric builder	Experimental compound IL 759 (Atlas Chem. Industries, Inc.)
100-822	Carboxylated starch	Experimental compound OS starch (Akzo Huishoudelijke Produkten NV, The Hague, Holland)
100-823	Acrylic builder	Experimental compound Calnox 214DN (Aquaness Chem. Co.)
100-824	Acrylic builder	Experimental compound Calnox 231 (Aquaness Chem. Co.)
102-833	Carboxyethyl Acetone	GRI experimental compound prepared according to U.S. Patent 3,716,487
102-834	Carboxylated starch builder	Experimental compound starch 294-10 (Akzo Huishoudelijke Produkten NV, The Hague, Holland)
102-836	Fatty acid diethanolamide condensate surfactant	Superamide L9A
104-855	Laundry detergent	Commercial laundry detergent - purchased Washington, D.C.-1973 Dynamo (Colgate-Palmolive Co.)

Appendix C (Continued)

Code No.	Type	Identity
104-856	Sodium dodecylbenzene sulfonamodiethyl sulfate surfactant	ER AF594-37 (Eastern Utilization Research & Dev. Div. USDARS)
104-860	Hydroxylated acrylic copolymer builder	Experimental compound POCNA (DEGUSSA)
106-866	Maleic telomer builder	GRI experimental compound
106-871	Maleic homopolymer builder	GRI experimental compound
108-880	Sulfopropionate surfactant	ER AFP610-007 (Eastern Utilization Research & Dev. Div. USDARS)

APPENDIX D

Selected Recent Patents Relating to Phosphate-Free Household Laundering Detergents

A. Monomeric Builders

1. C.A., 77 (1972) 154319n N,N-Bis (βhyroxyethyl) - substituted amino acids as builders for detergents. Rempfer, Heinz; Grossman, Heinrich (Chemische Werke Huels A.-G.) Ger. Offen. 2,103,725, 10 August 1972, 7 pp.

2. C.A., 78 (1973) 60055s N-Substituted disodium aminodicarboxylates as builders for detergents. Rempfer, Heinz (Chemische Werke Huels A.-G.) Ger. Offen. 2,125,249, 30 November 1972, 11 pp.
   N-substituted aspartates and iminodiacetates.

3. C.A., 77 (1972) 138233v Phosphate-free detergent compositions. Kusashio, Koji; Ninagawa, Sadayoshi (Ajinomoto Co., Inc.) Japan Kokai 72 16,504, 2 September 1972, 5 pp.
   Glutamates and aspartates.

4. C.A., 77 (1972) 138238a Detergent formulations containing nonphosphorus builders. Yang, Meiling T. (Ethyl Corp.) U.S. 3,717,591, 20 February 1973, 6 pp.
   Sulfoethylimino diacetic acid.

5. C.A., 76 (1972) 142706c Detergent formulations containing water-soluble salts of N,N-bis(carboxymethyl)aspartic acid as builders. Yang, Meiling T. (Ethyl Corp.) U.S. 3,637,511, 25 January 1972, 5 pp.

6. C.A., 76 (1972) 129230y Detergent formulations containing nonphosphorus builders. Yang, Meiling T. (Ethyl Corp.) U.S. 3,635,829, 18 January 1972, 5 pp.
   Sulfopropylimino diacetic acid.

7. C.A., 78 (1973) 5729q Iminodisuccinic acid salts as detergent builders. Tate, Bryce E.; Berg, Rudolph G. (Pfizer Inc.) U.S. 3,697,453, 10 October 1972, 4 pp.

8. C.A., 77 (1972) 154302b Detergent. Unilever N.V. Neth. Appl. 72 00,084, 07 July 1972, 13 pp.
Pyridine dicarboxylic acid.

9. C.A., 77 (1972) 126134a Sulfonated alkanedicarboxylate builders for detergents. Von Praun, Ferdinand; Amende, Joachim (Chemische Werke Huels A.-G.) Ger. Offen. 2,143,010, 01 March 1973, 19 pp.
Sulfonated adipic acid and homologs.

10. C.A., 77 (1972) 138234w Sequestering agents and detergent builders. Lannert, Kent Philip (Monsanto Co.) Ger. Offen. 2,231,927, 18 January 1973, 21 pp.
2-oxa-1,3,3 butane tricarboxylic acid and analogs.

11. C.A., 78 (1973) 99507r α- Substituted-β -sulfosuccinic acids as detergent builders. Lamberti, Vincent (Unilever N.V.) Ger. Offen. 2,230,073, 28 December 1972, 37 pp.
α hydroxy - β sulfosuccinic acid and analogs.

12. C.A., 78 (1973) 113083h Phosphate-free detergents. Hentschel, Gerhard Oskar (Hentschel, Valter S.E.) Ger. Offen. 2,228,252, 21 December 1972, 12 pp.
monopropyl ester of malic acid

13. C.A., 78 (1973) 45433v Detergent builders. Konort, Mark D.; Lamberti, Vincent; Weil, Ira (Unilever N.V.) Ger. Offen. 2,220,295, 16 November 1972, 39 pp.
Carboxyalkyl substituted malic and aspartic acids.

14. U.S. Patent 3,692,685 Detergent compositions. Vincent Lamberti, Mark D. Konort and Ira Weil to Lever Brothers Company, September 18, 1972.
Carboxymethyloxysuccinic acid (CMOS).

15. C.A., 78 (1973) 45417t Detergent formulations. Lannert, Kent P. (Monsanto Co.) U.S. 3,704,320, 28 November 1972, 2 pp.
2,4-dioxapentane-1,3,3,5-tetracarboxylic acid.

16. C.A., 77 (1972) 11639y Enzymic detergents containing citrate builders. Mast, Roy Clark (Proctor and Gamble Co.) Ger. Offen. 2,161,779, 29 Jun 1972, U.S. Appl. 98,114, 14 December 1970; 40 pp.

17. C.A., 77 (1972) 166522m Built detergent formulations. Harken, Russell D. (Monsanto Co.) U.S. 3,689,418, 05 September 1972, 2 pp.
    Ethenetetracarboxylic acid.

18. Dutch Pat. Appl'n 70-17181, 24 November 1970, D. S. Conner and J. E. Thompson to the Proctor and Gamble Co. Built Detergent Composition. Corresponds to Belg. Pat. 759,283 and U.S. Serial No. 879,612.
    Mellitic Acid.

19. C.A., 77 (1972) 116399f Detergent builders. Benjamin, Lawrence; Connor, Daniel Stedman (Proctor and Gamble Co.) Ger. Offen. 2,161,768, 06 July 1972, 41 pp.
    Mellitic acid used with carbonate and silicate.

20. U.S. Patent 3,661,787 Saturated Aliphatic Dicarboxylic Acid Salts as Detergent Builders, George E. Brown, Jr. to the Pollutrol Group, May 9, 1972.
    Succinic and oxalic acids. Claims limited to potassium palmitate as the surfactant.

21. C.A., 77 (1972) 50565y Detergent builders. Lamberti, Vincent (Unilever N.V.) Ger. Offen. 2,150,544, 13 April 1972, 15 pp.
    Oxydiacetic acid.

22. C.A., 75 (1971) 111128r Phosphate-free builders for detergents. Konort, Mark D.; Lamberti, Vincent (Unilever N.V.) Ger. Offen. 2,057,259, 09 June 1971, 17 pp.
    Tetrahydrofuran tetracarboxylic acid.

23. C.A., 78 (1973) 5720e Tetrasodium tetrahydrofurantetracarboxylate builder for detergents. Jakobi, Guenter; Perner, Johannes (Henkel und Cie. G.m.b.H) Ger. Offen. 2,113,730, 28 September 1972, 29 pp.

24. U.S. Patent 3,580,852 Detergent formulations containing Tetrahydrofuran 2,3,4,5 - Tetracarboxylic Acid Salts as Builders. Meiling T. Yang to Ethyl Corporation, May 25, 1971.

25. U. S. Patent 3,699,159 1,3,5-Trihydroxy-2,4,6-benzene tricarboxylic acid and water soluble salts thereof. Daniel S. Conner and Harry Karl Krummel to the Proctor and Gamble Company, October 17, 1972.

26. C.A., 77 (1972) 128512a Phenolic calcium-complexing agents for detergents. Conner, Daniel Steadman; Krummel, Harry Karl (Procter and Gamble Co.) Ger. Offen. 2,164,872, 20 July 1972.
    1,3,5-trisulfo-2,4,6-trihydroxy benzene and 1,3,5-tricarboxy-2,4,6-trihydroxy benzene.

27. C.A., 77 (1972) 128511z Tetracarboxylic acid detergents. Cummins, Richard Williamson; Lancelot, Charles Julian (FMC Corp.) Ger. Offen. 2,165,773 20 July 1972, 26 pp.
    Ethane tetracarboxylic acid and butane-1,2,3,4-tetracarboxylic acid. Stated to be biodegradable.

28. U.S. Patent 3,635,830 Detergent compositions containing oxydisuccinic acid salts as builders. Vincent Lamberti and Mark D. Konort to Lever Brothers Company, January 18, 1972.

29. Ger. Offen. 1,926,422 M. D. Konort and V. Lamberti to Unilever N.V., 4 December 1969, Detergent compositions. Corresponds to Fr. Application 2,009,946.
    Oxydisuccinic acid.

30. U. S. Patent 3,686,124 Carboxymethylated derivates of di- and tri-saccharide compounds and detergent compositions containing them. Warren I. Lyness and James E. Thompson to the Proctor and Gamble Co., August 22, 1972.
    Carboxymethylated sucrose, lactose, and raffinose.

31. U.S. Patent 3,669,890 Builders for synthetic detergent compositions based on carboxyethyl derivatives of polyalcohols. Martin M. Tessler and Morton W. Rutenberg to National Starch and Chemical Corporation, June 13, 1972.
    Carboxyethyl pentaerythritol.

32. U.S. Patent 3,725,290 Oxyacetic acid compounds as builders for detergent compositions. Douglas Carlyle Nelson and Edward Andrew Knaggs to Stepan Chemical Company, April 3, 1973.
    Carboxymethyl ethers of tri- and tetraglycols, pentaerythritol, etc.

33. C.A., 77 (1972) 77086e Builders for synthetic detergent compositions based on carboxyethyl derivatives of polyalcohols. Tessler, Martin M.; Rutenberg, Morton W. (National Starch and Chemical Corp.) U.S. 3,669,890, 13 June 1972, 5 pp.
    Carboxyethyl ethers of pentaerythritol and gluconic acid.

34. C.A., 76 (1973) 113105s Sulfosuccinate salt-containing detergents. Rempfer, Heinz; Schulze, Klaus (Chemische Werke Huels A.-G.) Ger. Offen. 2,136,360, 01 February, 1973, 11 pp.

Sulfosuccinic esters of fatty alcohol ethoxylates (surface active) used as builders for alkylbenzene sulfonates.

35. U.S. Patent 3,725,286 Detergent compositions. Robert Pettigrew to Lever Brothers Company, April 3, 1973.

Long chain succinic or malonic acids (surface active) used as builders for alkylbenzene sulfonates.

36. C.A., 78 (1973) 73947j Laundry detergent. Unilever N.V., Fr. 2,107,437, 09 June 1972, 10 pp.

Alpha sulfonated fatty acids as builders.

37. C.A., 77 (1972) 22028g Solid and liquid detergent compositions. Davies, James Francis; Gauterin, Charles R.; Ailbert, Philip A.; Griffiths, Storer C.C.; Griffiths, David W. L. (Unilever N.V.) Ger. Offen. 2,144,592, 16 March 1972, 12 pp.

Alpha sulfonated fatty acids used as builders for anionics or nonionics.

38. C.A., 77 (1972) 116400z Textile detergents. Davies, James Francis; Gauterin, Charles Rowland; Griffiths, David W. L.; Storer, Christopher Charles (Unilever N.V.) Ger. Offen. 2,161,726, 06 July 1972, 21 pp.

α sulfonated fatty acids (surface active) used as builders for alkylbenzene sulfonate.

39. C.A., 78 (1973) 113088p Phosphate-free detergents. Pettigrew, Robert; Tissington, Peter (Unilever N.V.) Ger. Offen. 2,232,414, 25 January 1973, 11 pp.

Sodium 2-hydroxy-n-tetradecanoate used as builder for alkylbenzene sulfonate.

40. C.A., 78 (1973) 31848x Laundry detergent. Davies, James Francis; Gilbert, Philip Alan, Thompson, Laurence (Unilever N.V.) Ger. Offen. 2,222,993, 16 November 1972, 23 pp. Corresponds to Belg. Patent 783,176.

Long chain alkane 1,2-disulfonates or 1,2-sulfonate-sulfinate (surface active) used as builders for alkylbenzene sulfonate.

41. C.A., 72 (1970) 14116r Taurine derivatives for replacing sodium tripolyphosphate in detergents. Lincoln, Robert M.; Meyers, Joseph Andrew, III; Sauer, Richard W. (Atlantic Richfield Co.) Fr. 1,556,816, 07 February 1969, 8 pp. Corresponds to U.S. 3,579,457, May 18, 1971.

    Long chain taurine derivatives (surface active) used with carbonate as builders for alkylbenzene sulfonate.

B. Polymeric Builders

1. U.S. Patent 3,308,067. Detergent compositions. Francis L. Diehl to Proctor and Gamble Co., March 7, 1967, 11 pp.

    Describes a range of polymeric aliphatic carboxylic acids. Homopolymers and copolymers of acrylic, maleic and itaconic acids used as builders for sulfonated or sulfated surfactants.

2. C.A., 77 (1972) 138227w (Alkyl)cyclopentene-maleic anhydride copolymer salt builder for detergents. Tsukuni, Hajime; Fujiki, Shun; Tsunoda, Teruo; Ocba, Yoichi (Hitachi Chemical Co., Ltd.), Ger. Offen. 2,238,275, 15 February 1973, 19 pp.

3. C.A., 78 (1973) 86336j Biodegradable builders for detergents. Kramer, J. K. (Shell Internationale Research Maatschappij N. V.) Neth. Appl. 72 05,685, 31 October 1972, 26 pp.

    Telomers of maleic acid. Methylisobutyl ketone and other materials as telogens.

4. C.A., 77 (1972) 154318m Composite maleic anhydride-vinyl methyl ether copolymer builders for detergents. Grifo, Richard Anthony (GAF Corp.) Ger. Offen. 2,200,779, 20 July 1972, 21 pp.

5. C.A., 78 (1973) 86308b New substitute for polyphosphate in detergents. Lauhus, Guenter P. (GAF G.m.b.H., Hamburg, Ger.). Seifen, Oele, Fette, Wachse 1972, 98 (26), 869-75 (Ger.)

    Copolymer maleic-methylvinyl ether.

6. C.A., 72 (1970) 33192d Textile detergent compositions. Arthur, Ralph P.; Belden, M. Joanne (Borg-Warner Corp.) Ger. Offen. 1,920,850, 20 November 1969, 14 pp.

    Maleic-butadiene copolymer.

7. C.A., 76 (1972) 74086y Polyelectroylte materials for use in detergents. Lancelot, Charles J.; Mackellar, Donald G. (FMC Corp.) Ger. Offen. 2,120,907, 11 November 1971, 26 pp.
Carbon monoxide-maleic copolymer.

8. C.A., 74 (1971) 77660a Poly (maleic acid) and salts for use as detergent builders and surfactants. Blumberg, John H.; MacKellar, Donald G. (FMC Corp.) U.S. 3,557,065, 19 January 1971, 3 pp.
Light-colored sodium polymaleate.

9. C.A., 76 (1972) 129218a Sodium polymaleate. Blumberg, John H.; Finley, Joseph H.; Rizzo, John J. (FMC Corp.) U.S. 3,637,609, 25 January 1972, 3 pp.
Refers to a bleached white sodium polymaleate.

10. C.A., 77 (1972) 90407e Sulfonated copolymers as detergent builders. Westernacher, Helmut; Schulze, Klaus (Chemische Werke Huels A.-G.) Ger. Offen. 2,056,813 25 May 1972, 15 pp.
Sulfonated ethylene-maleic copolymer.

11. C.A., 76 (1972) 74089b Sulfonated poly (maleic acid) detergent builders. Blumberg, John H.; Rizzo, John J.; MacKellar, Donald G. (FMC Corp.) U.S. 3,624,048 30 November 1971, 4 pp.

12. U.S. Patent 3,676,373 Detergent Compositions. Stanley C. Paviak to Gulf Research & Development Company, 11 July 1972.
Styrene-maleic copolymer of mol. wt. at least 3000.

13. U.S. Patent 3,730,913 Synthetic detergent compositions. Yoichi Oba, Chiharu Kato, Teruo Tsunoda, and Hajime Tsukuni, assignors to Hitachi, Ltd., and Hitachi Chemical Company, Ltd., May 1, 1973.
Copolymer of 3a,4,5,6,7,7a-hexahydro-4,7-methanoindene and maleic anhydride.

14. C.A., 77 (1972) 138247c Detergent compositions containing poly-electrolyte builders. Tokiwa, Fumikatsu; Imamura, Tetsuya (Kao Soap Co., Ltd.) Japan, Kokai 73,12,807, 17 February 1973, 5 pp.
C_{3-12} alkene-maleic copolymer. e.g. octene-maleic.

15. C.A., 77 (1972) 141726t Cleaning and soil-preventive compositions. Schomburg, Noel L., (Monsanto Co.) U. S. 3,679,592, 25 July 1972, 2 pp.
Maleic-ethylene copolymer half butyl ester.

16. C.A., 76 (1972) 115211f Detergent compositions. Arthur, Ralph P.; Belden, M. Joanne (Borg-Warner Corp.) Ger. Offen. 2,125,461, 02 December 1971, 22 pp.
Maleic-butadiene copolymer.

17. C.A., 78 (1973) 60040h Detergent polyelectrolyte builders. Martin, Preston Kuhn; Kelly, Richard Howard (Celanese Corp.) U.S. 3,706,672, 19 December 1972, 6 pp.
Polyacrylic acid of controlled mol. wt.

18. C.A., 78 (1973) 45424t Partial salts of polymerized aliphatic carboxylic acids, for use in detergents. Unilever N.V. Fr. 2,075,287, 12 November 1971, 18 pp.
Polyacrylic acid.

19. U.S. Patent 3,692,704 Method of Laundering Fabrics. James K. Stamm, Edwin R. Loder, Charles A. Brungs, and Herman Kerst to Chemed Corporation, September 19, 1972.
Mixture of polyacrylic acid and poly (N,N-dicarboxymethyl acrylamide).

20. C.A., 78 (1973) 113104r Sodium poly (α - hydroxyacrylate)-containing detergents. Wegemund, Bernd; Jakobi, Guenter (Henkel und Cie. G.m.b.H.) Ger. Offen. 2,136,672, 01 February 1973, 34 pp.

21. C.A., 78 (1973) 99517u Detergents and bleaches containing dispersible complex-forming mixtures. Batka, Heimold; Altenschoepfer, Theodor (Henkel und Cie. G.m.b.H.) Ger. Offen. 2,134,695, 25 January 1973, 28 pp.
Acrolein-acrylic copolymer.

22. C.A., 78 (1973) 99475d Poly (hydroxycarboxylates), a class of multiply applicable complexing agents. Haschke, Heinz; Morlock, Gerhard; Kuzel, Peter (Bereich Forsch. Chem., Degussa, Frankfurt/M., Ger.). Chem.-Ztg. 1972, 96(4), 199-207 (Ger).
The properties of the title compds., prepd. from salts of acrolein-acrylic acid copolymer by the Cannizzaro, reaction are described with respect to their application.

23. French Patent 2,083,006. Product for washing. Degussa. December 10, 1971.
    Acrolein-acrylic acid copolymer converted by Cannizaro reaction to allyl alcohol-acrylic copolymer.

24. U.S. Patent 3,629,121 Carboxylated starches as detergent builders. Ibrahim A. Eldib, December 21, 1971.

25. C.A., 78 (1973) 5672r Dicarboxy group-containing starch for detergents. Powers, Peter James; Reynolds, John Henry (Unilever N. V.) Ger. Offen. 2,213,955, 28 September 1972, 19 pp.
    Purified by treatment with sodium borohydride.

26. C.A., 75 (1971) 7765k Detergent composition. Unilever N.V. Neth. Appl. 70 12,380, 23 February 1971, 41 pp.
    Carboxylated starches and celluloses.

27. C.A., 77 (1972) 166520j Dicarboxymethyl starch detergent compositions. Cornelissens, Emery G. P.; Ploumen, Jan J. H. (Akzo G.m.b.H.) Ger. Offen. 2,207,917, 31 August 1972, Neth. Appl. 71 02,556, 25 February 1971, 12 pp.
    Dicarboxymethyl starch.

28. U.S. Patent 3,723,322 Detergent compositions containing carboxylated polysaccharide builders. Francis L. Diehl to The Procter & Gamble Company, March 27, 1973.
    Carboxylated alginic acid.

29. Starch-derived polyelectrolytes as builders in heavy duty detergent formulations. C. A. Wilham, T. A. McGuire, A. M. Mark and C. L. Mehltretter, J. Am. Oil Chemists Soc. 47, No. 12,522 (1970).

C. Surfactants stated to perform well without builders:

1. U.S. Patent 3,714,076. R. G. Anderson to Chevron Research Company, 30 January 1973.
    Viscinal disulfates.

2. U.S. Patent 3,686,098 Novel detergent composition. Ira Weil to Lever Brothers Company, August 22, 1972.
    Di-anionic sulfates and sulfonates.

3. C.A., 76 (1972) 87551w Heavy-duty laundry detergents containing polysulfonated alkyl phenols. Sharman, Samuel H.; Danzik, Mitchell (Chevron Research Co.) Ger. Offen. 2,121,675, 25 November 1971, 27 pp.

4. C.A., 77 (1972) 77078d 2,2-Disulfonated dialkyl sulfoxides and sulfones. Nooi, Jacobus Roelof (Lever Brothers Co.) U.S. 3,666,796, 30 May 1972, 5 pp.

5. C.A., 77 (1972) 63801x Alkyl alkoxybenzene disulfonates. Woo, Gar Lok (Chevron Research Co.) U.S. 3,663,609, 16 May 1972, 3 pp.

6. U.S. Patent 3,707,352 Linear Alkyl Hydrocarbyloxybenzene disulfonates. Gar Lok Woo to Chevron Research Company, December 26, 1972.

7. U.S. Patent 3,697,573 Linear alkylphenol sulfate-sulfonate phosphate-free detergent actives. Mitchell Danzik and Ralph House to Chevron Research Company, October 10, 1972.

8. Belg. Appl'n 774,270. Detergent disulfates of 2-hydrocarbon substituted butane diols. Anderson and Woo to Chevron Research Company, 9 January 1970.

9. C.A., 78 (1973) 126125y 1-(Sulfoalkyl)-4-undecylpyridinium inner salts as active detergents. Roberts, David William (Unilever N. V.) Ger. Offen. 2,238,371, 15 February 1973, 10 pp.
   Zwitterionic sulfonate.

10. C.A., 78 (1973) 60038p [(Alkylphenyl)dimethylammonio] propanesulfonates. Crabtree, Peter William; Vipond, Peter Wilfred (Unilever N. V.) Ger. Offen. 2,221,938, 23 November 1972, 12 pp.
    Zwitterionic sulfonate.

11. C.A., 78 (1973) 73967r Phosphate-free detergents containing glycol alkyl carboxymethyl ethers. Rempfer, Heinz; Amende, Joachim; Stache, Helmut; Grossman, Heinrich (Chemische Werke Huels A.-G.) Ger. Offen. 2,124,269, 30 November 1972, 15 pp.
    Polyether carboxylate

12. C.A., 78 (1973) 45416s Heavy-duty household detergent composition. Shane, Hugh J. S. (Hart Chemical Ltd.) Can. 912,395, 17 October 1972, 24 pp.
    Polyether carboxylate

13. C.A., 77 (1972) 166529u Detergent composition. Arai, Haruhiko; Minegishi, Yutaka; Takeuchi, Takeko (Kao Soap Co., Ltd.) Ger. Offen. 2,206,284, 31 August 1972, 17 pp.
    Polyether carboxylate

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2. U.S. Patent 3,708,428 Detergent compositions containing silica colloids. Louis McDonald, January 2, 1973.

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APPENDIX E

CHRONIC AQUATIC TOXICITY TESTS

A Summary of Chronic Test Procedures and Results for Test Sample 64-1

In order to establish a possible chronic toxicity profile for test sample 64-1 a number of biological tests were performed. Test sample 64-1 was tested against nine aquatic organisms and in addition histological studies of effects upon fish gill tissue and upon fish egg viability were also performed. The test exposure periods varied because of differences in the nature of the life cycle of the various test organisms. In addition, although most of the test organisms were exposed to two temperatures and three test dilution waters, not all the test organisms could be subjected to the desired temperatures and waters.

Three test dilution waters, a soft, a hard, and a high alkaline water, were synthesized using typical waters with these characteristics found in the United States. Two temperatures, 18°C and 30°C, were the test temperatures.

Three test concentrations were incorporated, derived from the acute tests of 64-1. These concentrations were, the highest concentration allowing 100% survival of the most sensitive organism over the 96-hour test period, a theoretical biologically safe concentration calculated by dividing the median tolerance concentration by one hundred, and a concentration mid-way between the two. The most sensitive test organism was the bluegill sunfish and the highest concentration allowing complete survival was 18 ppm. The other two test concentrations were 0.18 ppm and 8.7 ppm.

In all tests continuous flow techniques were used and the methods and procedures for the continuous flow procedures were the same as described in the acute test reports. The crustacean and insect were not tested acutely and these test procedures are described in this report.

The following chart lists the test organisms, length of exposure to 64-1, test dilution waters and test temperatures incorporated.

	Test Organism	Exposure Time	Dilution Water	Temp.
1.	Bluegill sunfish *Lepomis macrochirus* Raf.	60 days	soft hard alkaline	18°C 30°C
2.	Bullhead catfish *Ameiurus nebulosus*	60 days	soft hard alkaline	18°C 30°C

	Test Organism	Exposure Time	Dilution Water	Temp.
3.	Brook trout Salvelinus fontinalis	60 days	soft hard alkaline	18°C
4.	Pond snail Physa heterostropha Say	60 days	soft hard alkaline	18°C 30°C
5.	Gilled snail Amnicola limosa Say	60 days	soft hard alkaline	18°C 30°C
6.	Diatom Navicula seminulum var. hustedtii	14 days	soft hard alkaline	18°C
7.	Diatom Nitzschia palea	14 days	soft hard alkaline	18°C
8.	Crustacean Daphnia pulex	40 days	soft hard alkaline	18°C 30°C
9.	Insect mayfly Isonychia bicolor	25 days	soft hard alkaline	15°

Live fish egg studies were performed on the flagfish Jordanella floridae and histological gill investigations were performed on the bluegill sunfish and catfish gills exposed for sixty days to the test material 64-1.

Results

I. Bluegill sunfish, Lepomis macrochirus Raf.
   A. No death at any test concentration over the sixty day test period.
   B. No noticeable gross changes in feeding habits, general health or general behavior during the sixty day test period.

II. Bullhead catfish, Ameiurus nebulosus
   A. No death at any test concentration over the sixty day test period.
   B. No noticeable gross changes in feeding habits, general health or general behavior during the sixty day test period.

II. Brook trout, Salvelinus fontinalis
   A. No death at any test concentration over the sixty day test period.
   B. No noticeable gross changes in feeding habits, general health or general behavior during the sixty day test period.

IV. Pond snail, Physa heterostropha Say
   A. No death at any test concentration over the sixty day test period.
   B. Reproduction proceeded normally and one generation was produced during the sixty day test period.

V. Gilled snail, Amnicola limosa Say
   A. No death at any test concentration over the sixty day test period.
   B. No eggs were produced in test concentrations or controls during the sixty day test period. At the same time eggs were produced in the Amnicola culture tanks.

VI. The diatom Navicula seminulum var. hustedtii

Test Concentration	Alkaline Test Water	Soft Test Water	Hard Test Water
0.18 ppm	166% growth	108% growth	104% growth
8.7 ppm	115% growth	137% growth	132% growth
18.0 ppm	120% growth	71% growth	116% growth
Control	100% growth	100% growth	100% growth

VII. The diatom Nitzschia palea

Test Concentration	Alkaline Test Water	Soft Test Water	Hard Test Water
0.18 ppm	134% growth	144% growth	168% growth
8.7 ppm	106% growth	150% growth	132% growth
18.0 ppm	84% growth	124% growth	165% growth
Control	100% growth	100% growth	100% growth

VIII. Crustacean Daphnia pulex

Ten pregnant females were placed in the continuous flow test chambers containing the experimental dilutions and control. All tests were done in duplicate. The number of eggs in each brood pouch were counted and those not maturing were considered aborts. Young, born and living for 24 hours were counted and all but ten were removed from the test chambers, these ten were first generation test organisms. This process was repeated for three generations over a forty day test period.

Test Conc.	Alkaline Test Water	~~18%~~ 18 °C Soft Test Water	Hard Test Water
Control	100% survival of all test organisms with no aborts through three generations. A total of 228 eggs were produced.	100% survival of all test organisms with no aborts through three generations. A total of 232 eggs were produced.	100% survival of all test organisms with no aborts through three generations. A total of 244 eggs were produced.

Test Conc.	Alkaline Test Water	Soft Test Water	Hard Test Water
0.18 ppm	Same as control. A total of 243 eggs were produced.	Same as control. A total of 251 eggs were produced.	Same as control. A total of 229 eggs were produced.
8.7 ppm	100% survival of original 20 test organisms. 84 eggs were produced, 3% aborted and 5% of the young died. The 20 test organisms in the first generation produced 9 eggs and 100% aborted.	100% survival of original 20 test organisms. 74 eggs were produced, 1% aborted and 5% of the young died. The 20 test organisms in the first generation produced 10 eggs, and 100% aborted.	100% survival of original 20 test organisms. 87 eggs were produced, 2% aborted and 4% of young died. The 20 test organisms in the first generation produced no eggs.
18 ppm	0% survival of original 20 test organisms in 24 hours.	0% survival of original 20 test organisms in 4 days.	0% survival of original 20 test organisms in 5 days.
		30°C	
Control	100% survival of all test organisms with no aborts through three generations. A total of 243 eggs were produced.	100% survival of all test organisms with no aborts through three generations. A total of 241 eggs were produced.	100% survival of all test organisms with no aborts through three generations. A total of 265 eggs were produced.
0.18 ppm	Same as control. A total of 267 eggs were produced.	Same as control. A total of 278 eggs were produced.	Same as control. A total of 249 eggs were produced.
8.7 ppm	100% survival of original 20 test organisms. 96 eggs were produced, 2% aborted and 4.7% of the young died. The 20 test organisms in the first generation produced 12 eggs and 100% aborted.	100% survival of original 20 test organisms. 86 eggs were produced 1% aborted and 4% of young died. The 20 test organisms in the first generation produced 6 eggs, 100% aborted.	100% survival of original 20 test organisms. 98 eggs were produced, 1% aborted and 5% of young died. The 20 test organisms in the first generation produced no eggs.
18ppm	0% survival of original 20 test organisms in 24 hours.	0% survival of original 20 test organisms in 5 days.	0% survival of original 20 test organisms in 5 days.

IX. Insect *Isonychia bicolor*

Ten mature nymphs measuring about 1 to 1.5 cm in length not including tail were placed in the continuous flow test chambers containing the experimental dilutions and control. All tests were done in duplicate. The tests were allowed to proceed until all nymphs reached the sub imago and adult stage. Tests were conducted at 15°C. There were no deaths at any test concentration or control in any dilution water and all nymphs emerged successfully after 25 days of exposure.

X. Gill histology, sunfish and catfish

Five fish were sacrificed from each concentration at each temperature in each dilution water at the end of thirty days exposure and sixty days exposure. Gill slides were prepared according to techniques as stated in Cairns and Scheier, 1963. There were no apparent histological effects seen in either sunfish or catfish gills at concentrations of 0.18 or 8.7 ppm. At 18 ppm slight "clubbing" and adherence of gill lamellae were observed after 60 days of exposure in both sunfish and catfish. This effect could also be seen in the controls but its incidence appeared to be greater at 18 ppm. No epithelial stripping or capillary rupture was observed.

XI. Survival of *Jordanella* embryos and fry

Twenty-five, twenty-four hour old *Jordanella* eggs were placed in test chambers containing the test dilutions in soft, hard and alkaline water. Each test was done in triplicate and the test temperature was 30°C. Hatching occurred between the fourth and fifth day and the fry were observed for twelve days. The following chart lists average % survival after seventeen days.

Test Water	Control	0.18 ppm	8.7 ppm	18 ppm
soft	74.64%	72%	78%	62%
hard	78.84%	92%	76%	92%
alkaline	89.32%	92%	92%	84%

It should be noted that this fish does not naturally occur in soft water.

Summary:

The only profound effects of the test material at the experimental concentrations appear to be its stimulatory effect upon diatom growth at all concentrations and its extremely toxic effect upon *Daphnia* at the 8.7 ppm and 18 ppm levels. We are proceeding with high temperature diatom tests after having received two species of diatoms able to withstand the 30°C test temperature.

Literature Cited

Cairns, Jr., J. , and Scheier, A. "The Acute and Chronic Effects of Standard Sodium Alkyl Benzene Sulfonate Upon the Pumpkinseed Sunfish, *Lepomis gibbosus* (Linn.) and the Bluegill Sunfish *L. macrochirus* Raf." Proc. 17th Industrial Waste Conf. Eng. Ext. Ser. Series No. 112 Purdue University, 1963.

A Summary of Chronic Test Procedures and Results for Test Sample 86-700 (AATCCWOB)

In order to establish a possible chronic toxicity profile for test sample 86-700, a number of biological tests were performed. Test sample 86-700 was tested against nine aquatic organisms and in addition histological studies of effects upon fish gill tissue and upon fish egg viability were also performed. The test exposure periods varied because of differences in the nature of the life cycle of the various test organisms. In addition, although most of the test organisms were exposed to two temperatures and three test dilution waters, not all the test organisms could be subjected to the desired temperatures and waters.

Three test dilution waters--a soft, a hard, and a high alkaline water--were synthesized using typical waters with these characteristics found in the United States. Two temperatures--18°C and 30°C--were the test temperatures, except for the insect tests which were done at 15°C.

Three test concentrations were incorporated, derived from the acute tests of 86-700. These concentrations were (1) the highest concentration allowing 100% survival of the most sensitive organism over the 96-hour test period, (2) a theoretical biologically safe concentration calculated by dividing the median tolerance concentration by one hundred, and (3) a concentration mid-way between the two. The most sensitive test organism was the bluegill sunfish and the highest concentration allowing complete survival was 13.5 ppm. The other two test concentrations were 6.5 ppm and 0.153 ppm.

In all tests continuous flow techniques were used and the methods and procedures for the continuous flow procedures were the same as described in the acute test reports. The crustacean and insect were not tested acutely, and these test procedures are described in this report.

The following chart lists the test organisms, length of exposure to 86-700, test dilution waters, and test temperatures.

Test Organism	Exposure Time	Dilution Water	Temp.
1. Bluegill sunfish *Lepomis macrochirus* Raf.	60 days	soft hard alkaline	18°C 30°C

	Test Organism	Exposure Time	Dilution Water	Temp.
2.	Bullhead catfish *Ameiurus nebulosus*	60 days	soft hard alkaline	18°C 30°C
3.	Brook trout *Salvelinus fontinelis* Mitchell	60 days	soft hard	18°C
4.	Pond snail *Physa heterostropha* Say	60 days	soft hard alkaline	18°C 30°C
5.	Gilled snail *Amnicola limosa* Say	60 days	soft hard alkaline	18°C 30°C
6.	Diatom *Navicula seminulum* var. *hustedtii* Patr.	14 days	soft hard alkaline	18°C
7.	Diatom *Gomphonema parvulum*	14 days	soft hard alkaline	18°C
8.	Crustacean *Daphnia pulex*	40 days	soft hard alkaline	18°C 30°C
9.	Insect (mayfly) *Isonychia bicolor*	25 days	soft hard alkaline	15°C

Histological gill investigations were performed on the bluegill sunfish and catfish gills exposed for sixty days to the test material 86-700.

RESULTS

I. Bluegill sunfish, *Lepomis macrochirus* Raf.

- A. No death at any test concentration over the sixty-day test period.
- B. No noticeable gross changes in feeding habits, general health, or general behavior during the sixty-day test period.

II. Bullhead catfish, *Ameiurus nebulosus*

- A. No death at any test concentration over the sixty-day test period.
- B. No noticeable gross changes in feeding habits, general health, or general behavior during the sixty-day test period.

III. Brook trout, *Salvelinus fontinalis* Mitchell

- A. No death at any test concentration over the sixty-day test period.
- B. No noticeable gross changes in feeding habits, general health, or general behavior during the sixty-day test period.

IV. Pond snail, *Physa heterostropha* Say

- A. No death at any test concentration over the sixty-day test period.
- B. Reproduction proceeded normally, and one generation was produced during the sixty-day test period.

V. Gilled snail, *Amnicola limosa* Say

- A. No death at any test concentration over the sixty-day test period.
- B. Eggs were produced in all test concentrations, but no hatching was observed.

VI. The diatom *Navicula seminulum* var. *hustedtii* Patr.

Test Concentration	Alkaline Test Water	Soft Test Water	Hard Test Water
0.153 ppm	147.4% growth	105.6% growth	153.6% growth
6.5 ppm	333.3% growth	177.8% growth	139.3% growth
13.5 ppm	284.4% growth	130.9% growth	139.3% growth
Control	100% growth	100% growth	100% growth

VII. The diatom, *Gomphonema parvulum*

0.153	170.4% growth	58.5% growth	140.5% growth
6.5 ppm	199.1% growth	72.1% growth	154.5% growth
13.5 ppm	162.1% growth	115.3% growth	140.4% growth
Control	100% growth	100% growth	100% growth

VIII. Crustacean, *Daphnia pulex*

Ten pregnant females were placed in the continuous flow test chambers containing the experimental dilutions and control. All tests were done in duplicate. The number of eggs in each brood pouch were counted and those not maturing were considered aborts. Young, born and living for 24 hours, were counted and all but ten were removed from the test chambers. These ten were first generation test organisms. This process was repeated for three generations over a forty-day test period.

18°C

Test Conc.	Alkaline Test Water	Soft Test Water	Hard Test Water
Control	100% survival of all test organisms with no aborts through 3 generations. Total of 241 eggs were produced.	100% survival of all test organisms with no aborts through 3 generations. Total of 256 eggs were produced.	100% survival of all test organisms with no aborts through 3 generations. Total of 233 eggs were produced.
0.153 ppm	Same as control. A total of 236 eggs were produced.	Same as control. A total of 240 eggs were produced.	Same as control. A total of 247 eggs were produced.
6.5 ppm	80% survival, 1st generation test organisms; 94 eggs produced, 9.5% aborted, 14% young died. 85% survival, 2nd generation; 30 eggs produced, 26.3% aborted, 31.5% young died. 90% survival, 3rd generation; 27 eggs produced, 35.7% aborted, 50% young died.	90% survival, 1st generation test organisms; 86 eggs produced, 7% aborted, 20% young died. 80% survival, 2nd generation; 29 eggs produced, 31.2% aborted, 37.5% young died. 85% survival, 3rd generation; 22 eggs produced; 50% aborted, 30% young died.	85% survival, 1st generation test organisms; 63 eggs produced, 4.7% aborted, 17% young died. 90% survival, 2nd generation; 31 eggs produced, 26.3% aborted, 33.3% young died. 85% survival, 3rd generation; 17 eggs produced; 30% aborted, 50% young died.
13.5 ppm	0% survival, 1st generation test organisms in 10 days. 24 eggs produced, 9% aborted, no young born.	0% survival, 1st generation test organisms in 6 days. 18 eggs produced, 6.3% aborted, no young born.	0% survival, 1st generation test organisms in 11 days. 23 eggs produced, 7.4% aborted, no young born.

30°C

Test Conc.	Alkaline Test Water	Soft Test Water	Hard Test Water
Control	100% survival of all test organisms with no aborts through 3 generations. Total of 231 eggs were produced.	100% survival of all test organisms with no aborts through 3 generations. Total of 210 eggs were produced.	100% survival of all test organisms with no aborts through 3 generations. Total of 254 eggs were produced.
0.153 ppm	Same as control. A total of 225 eggs were produced.	Same as control. A total of 163 eggs were produced.	Same as control. A total of 239 eggs were produced.
6.5 ppm	85% survival, 1st generation test organisms; 96 eggs produced, 3.1% aborted, 4.8% young died. 85% survival, 2nd generation; 34 eggs produced, 0% aborted, 31.8% young died. 100% survival, 3rd generation; 10 eggs produced, 20% aborted, 42.9% young died.	80% survival, 1st generation test organisms; 38 eggs produced, 10.5% aborted, 13.1% young died. 50% survival, 2nd generation. No eggs produced in remaining test organisms of 2nd generation.	85% survival, 1st generation test organisms; 101 eggs produced, 3.9% aborted, 11.3% young died. 85% survival, 2nd generation; 21 eggs produced, 0% aborted, 42.1% young died. 95% survival, 3rd generation; 19 eggs produced, 15.5% aborted, 0% young died.
13.5 ppm	0% survival, 1st generation test organisms after 9 days. 42 eggs produced, 16.6% aborted, 100% young died.	0% survival, 1st generation test organisms after 7 days. 24 eggs produced, 25% aborted, no young born.	0% survival, 1st generation test organisms after 13 days. 35 eggs produced, 20% aborted, no young born.

IX. Insect, *Isonychia bicolor*

Ten mature nymphs measuring about 1 to 1.5 cm in length, not including tail, were placed in the continuous flow test chambers containing the experimental dilutions and control. All tests were done in duplicate. The tests were allowed to proceed until all nymphs reached the sub-imago and adult stage. Tests were conducted at 15°C. There were no deaths at any test concentration or control in any dilution water and all nymphs emerged successfully after 25 days of exposure.

X. Gill Histology--sunfish and catfish

Five fish were sacrificed from each concentration at each temperature in each dilution water at the end of thirty days' exposure and sixty days' exposure. Gill slides were prepared according to techniques outlined in Cairns and Scheier (1963).

Histological effects were seen at all concentrations in all dilution waters at the two test temperatures. At 30 days small amounts of epithalial stripping could be detected in both bluegills and catfish in all dilution waters and temperatures at all three concentrations. The intensity of the stripping varied directly as the test concentration increased. At 0.153 ppm approximately one-third of the examined gills showed some epithelial stripping, while 75% of the 6.5 ppm gills showed effects. Almost all the 13.5 ppm gills showed some epithelial stripping after 30 days' exposure. After 60 days' exposure about 50% of the 0.153 ppm gills showed effects in all dilution water and temperatures. Almost all 6.5 ppm and 13.5 ppm gills were affected after 60 days' exposure.

XI. Survival of *Jordanella* embryos and fry

Twenty-five 24-hour old *Jordanella* eggs were placed in test chambers containing the test dilutions in soft, hard, and alkaline water. Each test was done in triplicate and the test temperature was 30°C. Hatching occurred between the fourth and fifth day, and the fry were observed for twelve days. The following chart lists average percent survival after seventeen days.

Test Water	Control	0.153 ppm	6.5 ppm	13.5 ppm
Soft	94.5%	96.0%	80.0%	69.3%
Hard	88.0%	82.6%	86.6%	78.6%
Alkaline	92.0%	89.3%	76.0%	81.3%

It should be noted that this fish does not naturally occur in soft water.

SUMMARY

The marked effects of this test material appeared to be its stimulatory effect upon diatom growth at almost all concentrations, its toxic effect upon Daphnia at the 6.5 ppm and 13.5 ppm level, and histological changes in gill tissue at all concentrations. All effects were, for the most part, independent of dilution water or temperature.

LITERATURE CITED

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